Electronic Supplementary Material (ESI) for Chemical Communications

Asymmetric domino synthesis of indanes bearing four contiguous stereocentres catalyzed by sub-mol% loadings of a squaramide in minutes

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Supporting Information

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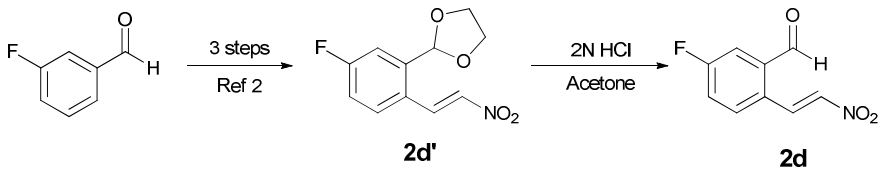
General Information

All reactions were performed in oven-dried glassware. Starting materials and reagents were purchased directly from commercial suppliers (Acros, Sigma Aldrich, TCI Europe and ABCR) and used without further purifications unless otherwise stated. All solvents were distilled, purified and dried according to standard procedures. $CHCl_3$ used in this methodology was analytical reagent grade $CHCl_3$ stabilized with amylene from Fisher Scientific. Analytical TLC were performed using SIL G-25 UV_{254} from MACHERY NAGEL and visualized either with ultraviolet radiation at 254 nm. 3 Å powdered molecular sieves were activated and dried under high vacuum using a heat gun before usage.

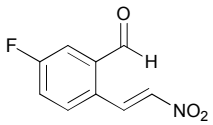
^1H and ^{13}C NMR spectra were recorded at ambient temperatures on a Varian Innova 600, Varian Innova 400 or a Varian Mercury 300 instrument with tetramethylsilane as the internal standard. Chemical shifts for ^1H-NMR and ^{13}C-NMR are reported in parts per million (ppm), with coupling constants reported in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet and m = multiplet. Mass spectra were acquired on a Finnigan SSQ7000 (EI 70 eV) spectrometer, high resolution mass spectra (HRMS) on a Finnigan MAT 95 and high resolution ESI spectra on a ThermoFisher Scientific LTQ-Orbitrap XL. IR spectra were taken on a PerkinElmer Spectrum 100 FT-IR Spectrometer. Elemental analyses were performed with a Vario EL elemental analyzer. Analytical HPLC were carried out either on a Hewlett-Packard 1050 Series instrument or Agilent 1100 instrument using chiral stationary phases. Optical rotation values were measured on a Perkin-Elmer 241 polarimeter. Substrates **1**[1] and substrates **2a-c** were synthesized using known literature procedures.[2,3]

Synthesis of Substrates



2d' **2d**

(*E*)-5-fluoro-2-(2-nitrovinyl)benzaldehyde (2d)



2d

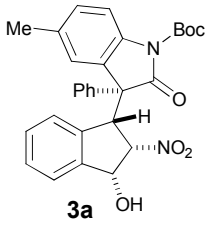
To a solution of **2d'**[2] (3.23 g, 13.5 mmol, 1 equiv.) dissolved in 57 mL of acetone was added 2N HCl (27 mL, 54 mmol, 4 equiv.) and the solution was stirred for at RT for 3 h. Upon completion of the reaction, excess distilled water was added to the flask and the precipitated solid was filtered, washed with pentane and dried under high vacuum to yield a yellow solid (1.67 g, 64%). Mp = 68-71 °C; IR (Capillary): 3370, 3102, 3071, 2864, 2753, 2295, 2147, 2109, 1924, 1789, 1692, 1631, 1596, 1555, 1492, 1378, 1341, 1251, 1194, 1151, 1096, 951, 883, 832, 781, 721, 673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 10.19 (s, 1H), 8.85 (d, *J* = 13.6 Hz, 1H), 7.66–7.62 (m, 2H), 7.46 (d, *J* = 13.6 Hz, 1H), 7.39 (ddd, *J* = 8.6, 7.8, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = ^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.3, 164.5 (d, *J* =

256.6 Hz), 139.9 (d, *J* = 24.7 Hz), 136.6 (d, *J* = 6.0 Hz), 135.2 (d, *J* = 20.3 Hz), 130.9 (d, *J* = 8.1 Hz), 127.5 (d, *J* = 3.7 Hz), 121.6 (d, *J* = 22.0 Hz), 120.8 (d, *J* = 22.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = − 106.06 ppm; MS (EI, 70 ev): *m/z* (%) 149.1 (100) $[M\text{-}NO_2]^+$, 120.1 (20), 101.1 (42); Anal. Calcd. for $C_9H_6FNO_3$: C, 55.39; H, 3.10; N; 7.18. Found: C, 55.39; H, 3.06; N, 7.16.

General Procedure for the Michael/Henry Domino Reaction

To a vial containing the *o*-benzaldehyde nitroolefin **2a-d** (0.50 mmol, 1 equiv.), Boc-protected oxindole **1** (0.55 mmol, 1 equiv.) and squaramide catalyst **10** (2.50 μmol, 0.005 equiv., 0.5 mol%) was added analytical reagent grade $CHCl_3$ (0.3 mL) and allowed to stir at room temperature for 45 min at ambient conditions. The crude mixture was then transferred to a flash column and purified by flash column chromatography to yield the pure products.

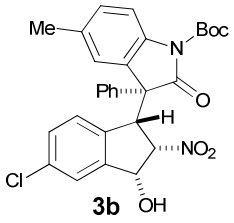
tert-Butyl 3-((*1S,2S,3R*)-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (3a)



3a

Compound **3a** was isolated as a diastereomeric mixture (≥20:1 d.r.) by flash column chromatography (3:1 Pentane:Et_2O) to yield a white solid (233 mg, 93%); Mp = 159 °C; $[\alpha]_D^{24}$ = + 190.7 (c = 0.70, $CHCl_3$), 93% ee (major diastereomer); IR (Capillary): 3477, 3251, 3089, 2980, 2926, 2322, 2180, 2063, 1922, 1743, 1601, 1550, 1488, 1336, 1247, 1148, 1066, 987, 913, 876, 819, 737, 664 cm^{-1}; ^{1}H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 7.58 (d, *J* = 8.4 Hz, 1H), 7.32-7.41 (m, 5H), 7.20-7.24 (m, 2H), 7.14-7.19 (m, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.90 (s, 1H), 5.46 (m, 1H), 5.39 (dd, *J* = 7.8, 2.4 Hz, 1H), 5.32 (d, *J* = 1.8 Hz, 1H), 2.36 (bs, 1H), 2.30 (s, 3H), 1.63 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 175.4, 149.0, 141.3, 138.0, 137.8, 137.2, 134.3, 130.2, 129.8, 129.5, 129.4, 128.9, 127.9, 127.3, 124.9, 124.8, 124.4, 115.4, 91.9, 85.0, 75.7, 60.2, 57.4, 28.3, 21.4 ppm; MS (ESI, pos): *m/z* (%) 539.158 (20) $[M+K]^+$, 523.184 (95) $[M+Na]^+$; HRMS (ESI): calcd. for $C_{29}H_{28}O_6N_2Na$: 523.1840, found: 523.1834; HPLC (major diastereomer): t_R 17.97 min (major) 22.11 min (minor), n-heptane/isopropanol, 95:5, 1.00 mL/min, Chiralcel-OD column.

tert-Butyl 3-((*1S,2S,3R*)-5-chloro-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (3b)

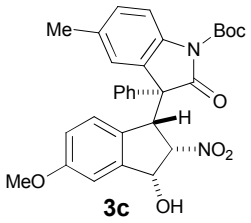


3b

Compound **3b** was isolated as a diastereomeric mixture (≥20:1 d.r.) by flash column chromatography (3:1 Pentane:Et_2O) to yield a white solid (239 mg, 89 %); Mp = 169 °C; $[\alpha]_D^{24}$ = + 142.5 (c = 0.74, $CHCl_3$), 90% ee (major diastereomer); IR (Capillary): 3464, 2979, 1742, 1557, 1480, 1366, 1228, 1143, 896, 826, 704 cm^{-1}; ^{1}H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 7.61 (d, *J* = 8.4 Hz, 1H), 7.31-7.40 (m, 5H), 7.21 (m, 1H), 7.13 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.92 (s, 1H), 5.44 (app d, *J* = 7.8 Hz, 1H), 5.36 (dd, *J* = 7.8, 2.4 Hz, 1H), 5.24 (d, *J* = 1.8 Hz, 1H), 2.49 (bs, 1H), 2.32 (s, 3H), 1.63 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 175.2, 148.8, 143.3, 137.7, 137.0, 136.5, 135.2, 134.5, 130.5, 130.0, 129.5, 129.0, 127.8, 127.1, 125.7, 125.2, 124.8, 115.6, 91.9, 85.2, 75.2, 60.0, 56.9, 28.3, 21.4 ppm; MS (EI, 70 eV):

m/z (%) 534.0 (1) $[M]^+$, 433.6 (3) $[M-Boc]^+$, 322.4 (20), 222.8 (100), 193.6 (30); HRMS (ESI): calcd. for $C_{29}H_{27}O_6N_2ClNa$: 557.1450, found: 557.1455; HPLC (major diastereomer): t_R 7.34 min (major) 8.66 min (minor), n-heptane/isopropanol, 90:10, 0.50 mL/min, Chiralpak-IC column.

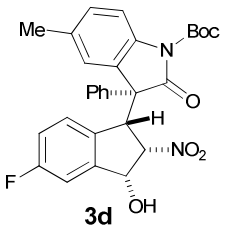
tert-Butyl 3-((*1S,2S,3R*)-3-hydroxy-5-methoxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (3c)



3c

Compound **3c** was isolated as a diastereomeric mixture (≥20:1 d.r.) by flash column chromatography (3:1 Pentane:Et_2O) to yield a pale yellow solid (252 mg, 95 %); Mp = 163 °C; $[\alpha]_D^{24}$ = + 157.7 (c = 0.73, $CHCl_3$), 90% ee (major diastereomer); IR (Capillary): 3469, 2949, 1741, 1614, 1557, 1486, 1366, 1246, 1147, 1030, 822, 699 cm^{-1}; ^1H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 7.60 (d, *J* = 8.4 Hz, 1H), 7.31-7.40 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.92 (s, 1H), 6.67-6.73 (m, 2H), 5.41 (d, *J* = 7.2 Hz, 1H), 5.38 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.22 (app s, 1H), 3.72 (s, 3H), 2.37 (bs, 1H), 2.32 (s, 3H), 1.63 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 175.4, 160.7, 149.0, 142.9, 137.9, 137.3, 134.3, 130.2, 129.7, 129.4, 128.8, 127.9, 127.4, 125.4, 124.8, 116.7, 115.4, 108.9, 92.4, 84.9, 75.6, 60.2, 56.9, 55.6, 28.3, 21.4 ppm; MS (ESI, pos): *m/z* (%) 553.196 (24) $[M+Na]^+$; HRMS (ESI): calcd. for $C_{30}H_{30}O_7N_2Na$: 553.1945, found: 553.1941; HPLC (major diastereomer): t_R 12.01 min (major) 13.19 min (minor), n-heptane/ethanol, 90:10, 0.50 mL/min, Chiralpak-IC column.

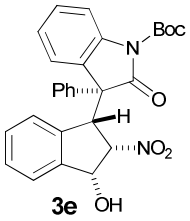
tert-butyl 3-((*1S,2S,3R*)-5-fluoro-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-5-methyl-2-oxo-3-phenylindoline-1-carboxylate (3d)



3d

Compound **3d** was isolated as a diastereomeric mixture (≥20:1 d.r.) by flash column chromatography (3:1 Pentane:Et_2O) to yield a white solid (239 mg, 83 %); Mp = 160 °C; $[\alpha]_D^{24}$ = + 172.7 (c = 0.66, $CHCl_3$), 90% ee (major diastereomer); IR (Capillary): 3467, 2980, 1741, 1607, 1557, 1487, 1367, 1312, 1248, 1146, 935, 876, 824, 729 cm^{-1}; ^1H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 7.60 (d, *J* = 8.4 Hz, 1H), 7.31-7.40 (m, 5H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.03 (m, 1H), 6.92 (app s, 1H), 6.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.86 (td, *J* = 8.4, 1.8 Hz, 1H), 5.40-5.46 (m, 1H), 5.37 (dd, *J* = 7.2, 1.8 Hz, 1H), 5.24 (app s, 1H), 2.46 (d, *J* = 8.4 Hz, 1H), 2.32 (s, 3H), 1.63 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 175.3, 163.3 (d, *J* = 256.7 Hz), 148.8, 143.6 (d, *J* = 7.85 Hz), 137.8, 137.0, 134.4, 133.5 (d, *J* = 2.42 Hz), 130.4, 129.5, 128.9, 127.9, 127.2, 126.0 (d, *J* = 8.61 Hz), 124.8, 117.2 (d, *J* = 22.8 Hz), 115.5, 111.9 (d, *J* = 23.1 Hz), 92.2, 85.2, 75.2, 60.1, 56.8, 28.3, 21.4; ^{19}F (564 MHz, $CDCl_3$, major diastereomer): δ = −112.1 ppm; MS (ESI, pos): *m/z* (%) 541.175 (50) $[M+Na]^+$; HRMS (ESI): calcd. for $C_{29}H_{27}O_6N_2FNa$: 541.1745, found: 541.1744; HPLC (major diastereomer): t_R 7.76 min (major) 9.02 min (minor), n-heptane/ethanol, 90:10, 0.50 mL/min, Chiralpak-IC column.

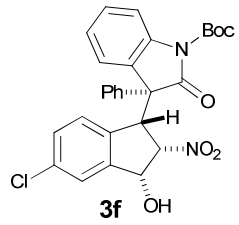
tert-butyl 3-((*1S,2S,3R*)-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-2-oxo-3-phenyl indoline-1-carboxylate (3e)



3e

Compound **3e** was isolated as a diastereomeric mixture (≥20:1 d.r.) by flash column chromatography (3:1 Pentane:Et_2O) to yield a white solid (209 mg, 86 %); Mp = 158 °C; $[\alpha]_D^{24}$ = + 215.2 (c = 0.61, $CHCl_3$), 90% ee (major diastereomer); IR (Capillary): 3475, 2981, 2931, 1739, 1606, 1556, 1466, 1369, 1316, 1286, 1250, 1146, 1106, 1066, 1024, 921, 838, 751, 695 cm^{-1}; ^1H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 7.71 (d, *J* = 8.4 Hz, 1H), 7.33-7.40 (m, 5H), 7.14-7.25 (m, 4H), 7.08-7.12 (m, 3H), 5.50 (d, *J* = 6.0 Hz, 1H), 5.39 (dd, *J* = 7.8, 2.4 Hz, 1H), 5.35 (d, *J* = 2.4 Hz, 1H), 2.39 (bs, 1H), 1.64 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 175.3, 148.9, 141.3, 140.2, 138.0, 137.1, 129.8, 129.7, 129.5, 129.4, 128.9, 127.9, 127.2, 124.9, 124.6, 124.3, 115.6, 91.9, 85.2, 75.6, 60.1, 57.5, 28.3 ppm; MS (ESI, pos): *m/z* (%) 509.167 (75) $[M+Na]^+$; HRMS (ESI): calcd. for $C_{28}H_{26}O_6N_2Na$: 509.1683, found: 509.1682; HPLC (major diastereomer): t_R 9.83 min (minor) 13.35 min (major), n-heptane/ethanol, 70:30, 0.50 mL/min, (*S*, *S*)-Whelk O1 column.

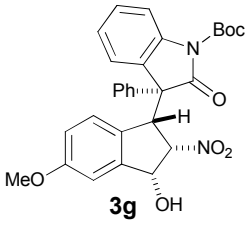
tert-butyl 3-((*1S,2S,3R*)-5-chloro-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (3f)



3f

Compound **3f** was isolated as a diastereomeric mixture (≥20:1 d.r.) by flash column chromatography (3:1 Pentane:Et_2O) to yield a white solid (240 mg, 92 %); Mp = 162 °C; $[\alpha]_D^{24}$ = + 168.3 (c = 0.55, $CHCl_3$), 90% ee (major diastereomer); IR (Capillary): 3469, 2980, 2926, 1745, 1605, 1557, 1471, 1314, 1252, 1146, 1089, 1022, 922, 879, 834, 759, 692 cm^{-1}; ^1H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 7.74 (d, *J* = 7.8 Hz, 1H), 7.32-7.40 (m, 5H), 7.27-7.31 (m, 1H), 7.20 (s, 1H), 7.10-7.16 (m, 3H), 6.99 (d, *J* = 7.8 Hz, 1H), 5.48 (d, *J* = 7.2 Hz, 1H), 5.36 (dd, *J* = 7.2, 1.8 Hz, 1H), 5.27 (d, *J* = 1.8 Hz, 1H), 2.54 (bs, 1H), 1.64 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 175.2, 148.8, 143.2, 140.1, 136.8, 136.4, 135.3, 130.1, 130.0, 129.6, 129.0, 127.8, 127.0, 125.6, 125.3, 124.8, 124.3, 115.8, 91.9, 85.5, 75.1, 59.9, 56.9, 28.3 ppm; MS (ESI, pos): *m/z* (%) 543.127 (10) $[M+Na]^+$; HRMS (ESI): calcd. for $C_{28}H_{25}O_6N_2ClNa$: 543.1293, found: 543.1289; HPLC (major diastereomer): t_R 3.79 min (major) 4.32 min (minor), n-heptane/ethanol, 90:10, 1.00 mL/min, Chiralpak-IC column.

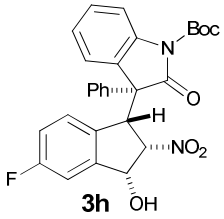
tert-butyl 3-((*1S,2S,3R*)-3-hydroxy-5-methoxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (3g)



3g

Compound **3g** was isolated as a diastereomeric mixture (≥20:1 d.r.) by flash column chromatography (3:1 Pentane:Et_2O) to yield a white solid (238 mg, 92 %); Mp = 155 °C; $[\alpha]_D^{25}$ = + 200.1 (c = 0.70, $CHCl_3$), 90% ee (major diastereomer); IR (Capillary): 3471, 2979, 2934, 1738, 1610, 1557, 1493, 1464, 1369, 1342, 1315, 1280, 1249, 1147, 1073, 1025, 924, 835, 759, 696, 656 cm^{-1}; ^1H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 7.74 (d, *J* = 7.8 Hz, 1H), 7.32-7.41 (m, 5H), 7.23-7.29 (m, 1H), 7.10-7.16 (m, 2H), 6.96-7.00 (m, 1H), 6.68-6.74 (m, 2H), 5.44 (app t, *J* = 8.4 Hz, 1H), 5.38 (dd, *J* = 7.2, 1.8 Hz, 1H), 5.25 (d, *J* = 1.2 Hz, 1H), 3.71 (s, 3H), 2.31-2.38 (m, 1H), 1.64 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 175.3, 160.8, 148.9, 142.9, 140.2, 137.1, 129.7, 129.5, 128.9, 127.9, 127.4, 125.3, 124.6, 124.4, 116.8, 115.7, 108.9, 92.3, 85.2, 75.5, 60.2,

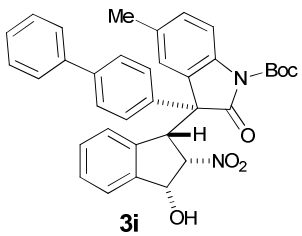
57.0, 55.6, 28.3 ppm; MS (ESI, pos): *m/z* (%) 555.152 (20) $[M+K]^+$; HRMS (ESI): calcd. for $C_{29}H_{28}O_7N_2Na$: 539.1789, found: 539.1787; HPLC (major diastereomer): t_R 11.39 min (minor) 15.93 min (major), n-heptane/ethanol, 70:30, 0.50 mL/min, (*S, S*)-Whelk O1 column.



***tert*-butyl 3-((*1S,2S,3R*)-5-fluoro-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-2-oxo-3-phenylindoline-1-carboxylate (3h)**

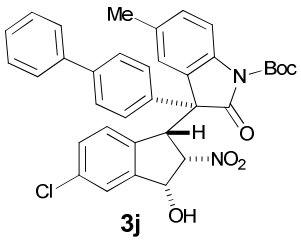
Compound **3h** was isolated as a diastereomeric mixture (≥20:1 d.r.) by flash column chromatography (3:1 Pentane:Et_2O) to yield a white solid (220 mg, 87 %); Mp = 149 °C; $[\alpha]_D^{25}$ = + 170.9 (c = 0.53, $CHCl_3$), 89 % ee (major diastereomer); IR (Capillary): 3472, 2980, 2930, 2287, 2021, 1779, 1740, 1608, 1558, 1486, 1369, 1342, 1317, 1252, 1145, 1107, 1065, 1023, 1000, 928, 875, 835, 757, 696, 656 cm^{-1}; ^1H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 7.73 (d, *J* = 8.4 Hz, 1H), 7.32-7.40 (m, 5H), 7.26-7.30 (m, 1H), 7.11-7.15 (m, 2H), 7.04 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.90 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.86 (td, *J* = 9.0, 2.4 Hz, 1H), 5.47 (app t, *J* = 7.2 Hz, 1H), 5.37 (dd, *J* = 7.2, 1.8 Hz, 1H), 5.26 (app s, 1H), 2.48 (d, *J* = 8.4 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 175.2, 163.6 (d, *J* = 256.7 Hz), 148.8, 143.6 (d, *J* = 8.3 Hz), 140.1, 136.8, 133.4, 129.9, 129.5, 129.0, 127.8, 127.1, 125.9 (d, *J* = 8.6 Hz), 124.7, 124.3, 117.2 (d, *J* = 23.0 Hz), 115.7, 111.9 (d, *J* = 22.8 Hz), 92.1, 85.4, 75.1, 60.1, 56.9, 28.3; ^{19}F (564 MHz, $CDCl_3$, major diastereomer): δ = −112.1 ppm; MS (EI, 70 eV): *m/z* (%) 504.0 (10) $[M]^+$, 447.8 (31), 404.4 (30) $[M-Boc]^+$, 387.0 (12), 338.8 (21), 327.2 (14), 308.7 (83), 294.0 (18), 283.4 (16), 253.2 (65), 234.5 (14), 207.9 (100), 189.4 (16), 179.2 (43), 164.6 (28), 151.4 (46), 126.4 (11), 54.6 (55); HRMS (ESI): calcd. for $C_{28}H_{25}O_6N_2FNa$: 527.1589, found: 527.1588; HPLC (major diastereomer): t_R 4.00 min (major) 4.38 min (minor), n-heptane/ethanol, 90:10, 1.00 mL/min, Chiralpak-IC column.

***tert*-butyl 3-([1,1'-biphenyl]-4-yl)-3-((1S,2S,3R)-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-5-methyl-2-oxoindoline-1-carboxylate (3i)**



Compound **3i** was isolated as a diastereomeric mixture (20:1 d.r.) by flash column chromatography (3:1 Pentane:Et_2O) to yield a white solid (251 mg, 87 %); Mp = 174 °C; $[\alpha]_D^{25}$ = + 166.7 (c = 0.63, $CHCl_3$), 98 % ee (major diastereomer); IR (Capillary): 3482, 3033, 2980, 2928, 1736, 1601, 1556, 1485, 1396, 1370, 1332, 1308, 1279, 1248, 1149, 1112, 1065, 1006, 950, 912, 821, 752, 696, 661 cm^{-1}; ^1H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 7.55-7.62 (m, 5H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.16-7.25 (m, 3H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.95 (s, 1H), 5.44-5.51 (m, 2H), 5.35 (app s, 1H), 2.36 (d, *J* = 9 Hz, 1H), 2.32 (app s, 3H), 1.64 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 174.4, 149.0, 141.7, 141.3, 140.3, 138.0, 137.9, 136.2, 134.4, 130.3, 129.8, 129.5, 129.1, 128.4, 128.1, 127.9, 127.3, 124.9, 124.8, 124.5, 115.4, 92.0, 85.0, 75.8, 60.1, 57.4, 28.3, 21.4 ppm; MS (ESI, pos): *m/z* (%) 599.211 (53) $[M+Na]^+$, 615.184 (99) $[M+K]^+$; HRMS (ESI): calcd. for $C_{35}H_{32}O_6N_2Na$: 599.2153, found: 599.2144; HPLC (major diastereomer): t_R 12.24 min (major) 14.03 min (minor), n-heptane/ethanol, 90:10, 0.70 mL/min, Chiralcel-OD column.

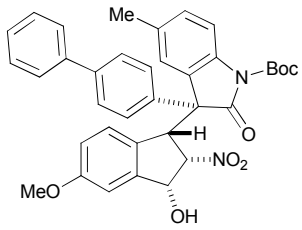
tert-butyl 3-([1,1'-biphenyl]-4-yl)-3-((1S,2S,3R)-5-chloro-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-5-methyl-2-oxoindoline-1-carboxylate (3j)



3j

Compound **3j** was synthesized using the general procedure with 1 mol% squaramide catalyst loading (20 min reaction time) and was isolated as a diastereomeric mixture (≥20:1 d.r.) by flash column chromatography (4:1 to 2:1 Pentane:Et_2O) to yield a white solid (254 mg, 83 %); Mp = 193 °C; $[\alpha]_D^{25}$ = + 135.4 (c = 0.55, $CHCl_3$), 99 % ee (major diastereomer); IR (Capillary): 3421, 2980, 2926, 2324, 2058, 1738, 1599, 1557, 1484, 1370, 1310, 1248, 1148, 1004, 956, 917, 894, 824, 756, 696 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$, major diastereomer): δ = 7.54-7.67 (m, 5H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.33-7.41 (m, 3H), 7.22 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.96 (s, 1H), 5.38-5.51 (m, 2H), 5.27 (app s, 1H), 2.46 (d, *J* = 8.8 Hz, 1H), 2.34 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, major diastereomer): δ = 175.2, 148.8, 143.3, 141.8, 140.2, 137.8, 136.4, 135.9, 135.3, 134.6, 130.6, 130.0, 129.1, 128.3, 128.2, 128.1, 128.0, 127.9, 127.3, 127.2, 125.8, 125.2, 124.7, 115.6, 92.0, 85.3, 75.2, 59.9, 56.9, 28.3, 21.4 ppm; MS (ESI, pos): *m/z* (%) 633.178 (22) $[M+Na]^+$, 649.152 (13) $[M+K]^+$; HRMS (ESI): calcd. for $C_{35}H_{31}O_6N_2ClNa$: 633.1763, found: 633.1769; HPLC (major diastereomer): t_R 20.86 min (major) 24.90 min (minor), n-heptane/ethanol, 95:5, 0.70 mL/min, Chiralcel-OD column.

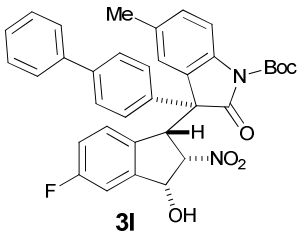
tert-Butyl 3-([1,1'-biphenyl]-4-yl)-3-((1*S*,2*S*,3*R*)-3-hydroxy-5-methoxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-5-methyl-2-oxoindoline-1-carboxylate (3k)



3k

Compound **3k** was isolated as a diastereomeric mixture (≥20:1 d.r.) after flash chromatography (2:1 Pentane:Et_2O) as white solid (282 mg, 92%). Mp = 169-172 °C; $[\alpha]_D^{24}$ = + 162.2 (c = 1.00, $CHCl_3$); 89% ee (major diastereomer); IR (Capillary): 3475, 2978, 2931, 2299, 2071, 1988, 1915, 1736, 1613, 1557, 1488, 1396, 1370, 1304, 1276, 1248, 1150, 1114, 1072, 1026, 957, 928, 900, 820, 757, 696 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major diastereomer): δ = 7.62 (d, *J* = 8.4 Hz, 1H), 7.60–7.55 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.36 (tt, *J* = 7.4, 1.0 Hz, 1H), 7.07 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.96 (s, 1H), 6.73–6.70 (m, 2H), 5.40-5.47 (m, 2H), 5.25 (app s, 1H), 3.72 (s, 3H), 2.39 (d, *J* = 8.5 Hz, 1H), 2.33 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ =175.4, 160.7, 148.9, 142.9, 141.5, 140.2, 137.8, 136.2, 134.3, 130.2, 129.6, 129.0, 128.3, 128.0, 127.9, 127.4, 127.2, 125.3, 124.7, 116.6, 115.4, 108.8, 92.3, 84.9, 75.6, 60.1, 56.8, 55.5, 28.3, 21.4.ppm; MS (ESI, pos): *m/z* (%) 629.226 (100) $[M+Na]^+$, 645.200 (76) $[M+K]^+$; HRMS (ESI): calcd for $C_{36}H_{34}N_2O_7K$: 645.2003, found: 645.1999; HPLC (major diastereomers): t_R 9.07 min (major), t_R 12.30 min (minor), n-heptane/ethanol, 90:10, 1.00 mL/min, Chiralcel-OD column.

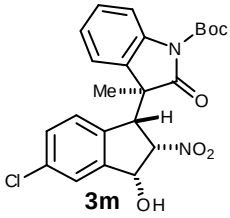
tert-Butyl 3-([1,1'-biphenyl]-4-yl)-3-((1*S*,2*S*,3*R*)-5-fluoro-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-5-methyl-2-oxoindoline-1-carboxylate (3l)



3l

Compound **3l** was isolated as a diastereomeric mixture (≥20:1 d.r.) after flash chromatography (4:1 Pentane:Et_2O) as pale orange solid (268 mg, 90%). Mp = 161-172 °C; $[\alpha]_D^{24}$ = + 175.5 (c = 1.00, $CHCl_3$); 91% ee (major diastereomer); IR (Capillary): 3824, 3457, 3032, 2979, 2928, 2721, 2500, 2287, 2080, 2009, 1984, 1912, 1739, 1608, 1558, 1487, 1448, 1395, 1370, 1309, 1249, 1148, 1112, 1050, 1004, 936, 873, 820, 757, 696, 659 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major diastereomer): δ =7.64–7.54 (m, 5H), 7.48–7.41 (m, 2H), 7.41–7.33 (m, 3H), 7.11–7.05 (m, 2H), 7.00–6.95 (m, 1H), 6.88 (ddd, *J* = 19.4, 8.4, 2.4 Hz, 2H), 5.47–5.42 (m, 2H), 5.28 (d, *J* = 8.5 Hz, 1H), 2.59 (s, 1H), 2.33 (s, *J* = 10.7 Hz, 3H), 1.63 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, major diastereomer): δ =175.3, 163.5 (d, *J* = 248.4 Hz), 148.8, 143.6 (d, *J* = 7.8 Hz), 141.7, 140.1, 137.7, 135.9, 134.5, 133.3 (d, *J* = 2.5 Hz), 130.4, 129.0, 128.2, 128.0, 127.86, 127.2, 127.2, 125.9 (d, *J* = 8.7 Hz), 124.7, 117.1 (d, *J* = 23.0 Hz), 115.5, 111.8 (d, *J* = 23.0 Hz), 92.2, 85.1, 75.2, 60.0, 56.7, 28.2, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$, major diastereomer): δ = −112.09 ppm; MS (ESI, pos): *m/z* (%) 617.207 (100) $[M+Na]^+$, 633.181 (76) $[M+K]^+$; HRMS (ESI): calcd for $C_{35}H_{31}FN_2O_6K$: 633.1798, found: 633.1799; HPLC (major diastereomers): t_R 14.16 min (major), t_R 17.14 min (minor), n-heptane/ethanol, 95:05, 1.00 mL/min, Chiralcel-OD column.

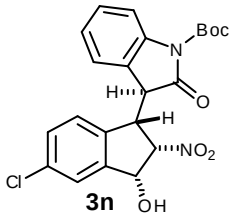
(*S*)-*tert*-Butyl 3-((1R,2S,3R)-5-chloro-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-3-methyl-2-oxoindoline-1-carboxylate (3m)



3m

Compound **3m** was isolated as a diastereomeric mixture (20:1 d.r.) after flash chromatography (2:1 Pentane:Et_2O) as a off-white solid (90 mg, 39%). Mp = 117 °C; $[\alpha]_D^{22}$ = + 19.5 (c = 0.55, $CHCl_3$); 39% ee (major diastereomer); IR (Capillary): 3455, 2979, 2928, 1776, 1607, 1557, 1472, 1368, 1346, 1315, 1285, 1252, 1145, 1092, 1012, 961, 881, 835, 757, 679, 616, 584, 552, 522 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major diastereomer): δ = 7.71 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.25 (app s, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.12-7.20 (m, 3H), 5.46 (d, *J* = 6.6 Hz, 1H), 5.40 (m, 1H), 4.25 (app s, 1H), 2.56 (bs, 1H), 1.65 (s, 9H), 1.64 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 177.0, 148.8, 143.5, 139.2, 136.1, 135.4, 129.7, 129.6, 129.4, 126.7, 125.0, 124.9, 122.7, 115.6, 91.2, 85.3, 75.1, 57.3, 51.0, 28.3, 22.7 ppm; MS (ESI, pos): *m/z* (%) 481.114 (66) $[M+Na]^+$; HRMS (ESI): calcd. for $C_{23}H_{23}O_6N_2ClNa$: 481.1137, found: 481.1136; HPLC (major diastereomers): t_R 7.92 min (minor), t_R 9.28 min (major), n-heptane/ethanol, 90:10, 1.00 mL/min, Daicel-OD column.

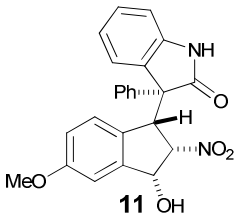
(*S*)-tert-butyl 3-((1S,2S,3R)-5-chloro-3-hydroxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-2-oxoindoline-1-carboxylate (3n)



3n

Compound **3n** was isolated as a diastereomeric mixture (12:1 d.r.) after flash chromatography (2:1 Pentane:Et_2O) as a off-white solid (99 mg, 44%). Mp = 73 °C; $[\alpha]_D^{22}$ = + 22.7 (c = 0.75, $CHCl_3$); % ee (major diastereomer); IR (Capillary): 3463, 2923, 2854, 2321, 2053, 1780, 1737, 1607, 1553, 1471, 1370, 1349, 1287, 1250, 1196, 1146, 1089, 1053, 1002, 878, 835, 753, 678 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, major diastereomer): δ = 7.86 (d, *J* = 8.4 Hz, 1H), 7.39-7.45 (m, 2H), 7.20-7.25 (m, 2H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 5.87 (t, *J* = 6 Hz, 1H), 5.56 (t, *J* = 6 Hz, 1H), 4.75 (m, 1H), 4.21 (d, *J* = 3 Hz, 1H), 2.61-2.67 (m, 1H), 1.57 (s, 9H) ; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.1, 148.8. 142.2, 140.6, 137.0, 135.1, 130.8, 129.6, 126.3, 125.3, 125.1, 125.0, 123.9, 115.7, 89.8, 85.2, 84.3 (minor), 73.9, 47.4, 47.1, 29.9 (minor), 28.3 (minor), 28.2 ppm; MS (ESI, pos): *m/z* (%) 467.099 (99) $[M+Na]^+$; HRMS (ESI): calcd. for $C_{22}H_{21}O_6N_2ClNa$: 467.0980, found: 467.0980; HPLC (major diastereomers): t_R 10.93 min (minor), t_R 19.28 min (major), n-heptane/isopropanol, 80:20, 0.70 mL/min, Chiralpak-IC column.

3-((1S,2S,3R)-3-hydroxy-5-methoxy-2-nitro-2,3-dihydro-1H-inden-1-yl)-3-phenyl indolin -2-one (11)



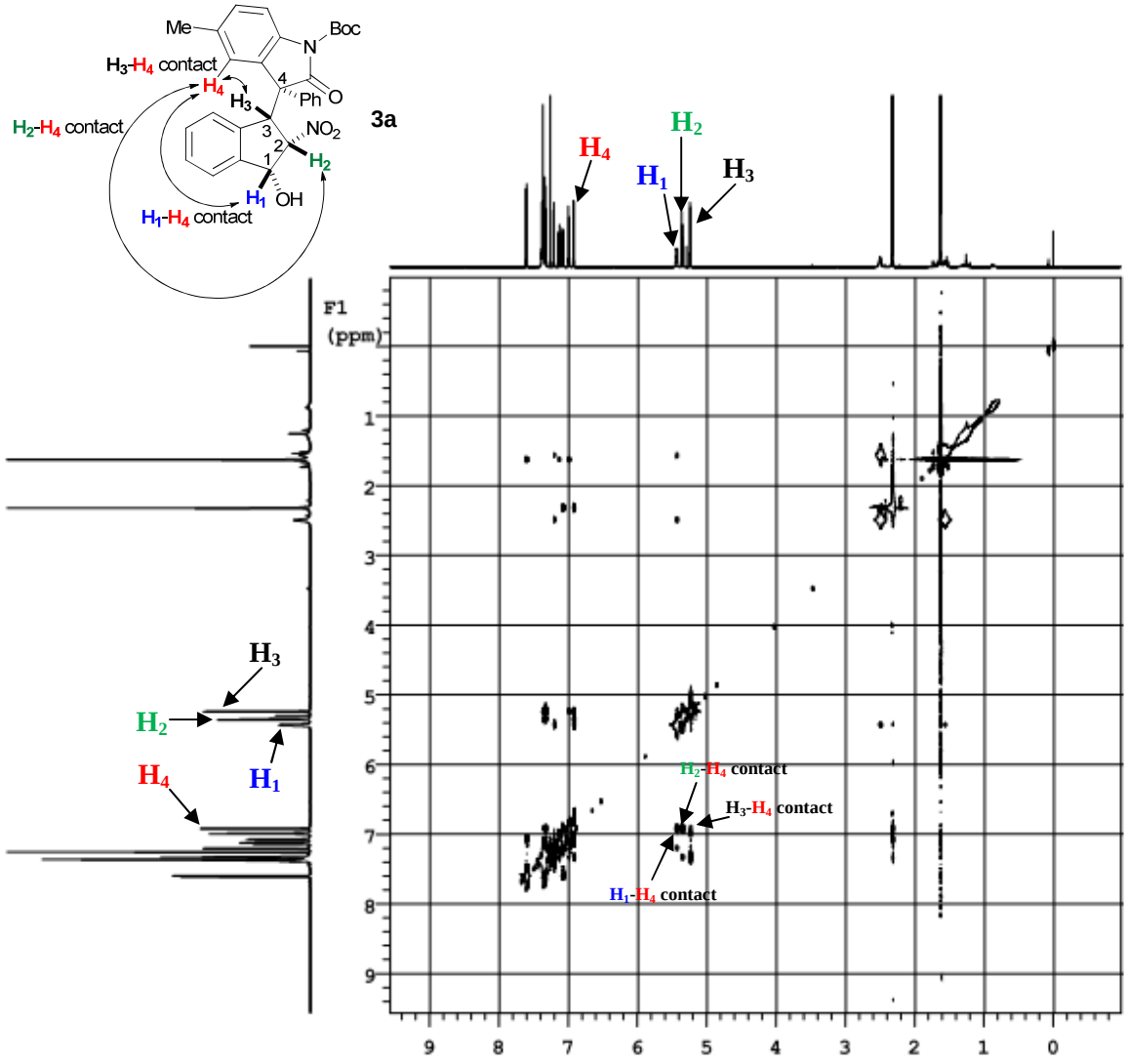
11

To a solution of **3g** (300 mg, 0.581 mmol, 1 equiv.) in CH_2Cl_2 (4 mL) was added trifluoroacetic acid (0.224 mL, 2.90 mmol, 5 equiv.) and stirred at RT for 2h. Distilled water was then added to quench the reaction and the product was extracted with CH_2Cl_2 (5 x 50 mL). The combined fractions are subsequently concentrated under vacuo and purified by flash column chromatography (2% MeOH in CH_2Cl_2) to yield a white solid (232 mg, 96%); Mp = 147 °C; $[\alpha]_D^{25}$ = + 193.9 (c = 0.79, $CHCl_3$), 88 % ee (major diastereomer, ≥20:1 d.r.); IR (Capillary): 3219, 2937, 2327, 2079, 1981, 1703, 1616, 1553, 1493, 1469, 1370, 1321, 1273, 1193, 1156, 1112, 1069, 1026, 967, 861, 832, 743, 697 cm^{-1}; ^1H NMR(600 MHz, $CDCl_3$, major diastereomer): δ = 8.18 (bs, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.31-7.38 (m, 3H), 7.11-7.19 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.68-6.75 (m, 3H), 5.50 (t, *J* = 7.2 Hz, 1H), 5.36 (dd, *J* = 7.8, 2.4 Hz, 1H), 5.19 (d, *J* = 2.4 Hz, 1H), 3.67 (s, 3H), 2.76 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$, major diastereomer): δ = 178.5, 160.6, 142.8, 140.8, 137.3, 130.0, 129.4, 129.3, 129.2, 128.6, 127.7, 125.7, 124.9, 122.9, 116.8, 110.8, 108.8, 92.4, 75.4, 60.1, 56.0, 55.5 ppm; MS (ESI, pos): *m/z* (%) 455.099 (98) $[M+K]^+$; HRMS (ESI): calcd. for $C_{24}H_{20}O_5N_2K$: 455.1004, found: 455.0988; HPLC (major diastereomer): t_R 13.46 min (minor) 26.46 min (major), n-heptane/ethanol, 70:30, 1.00 mL/min, Daicel-AD column.

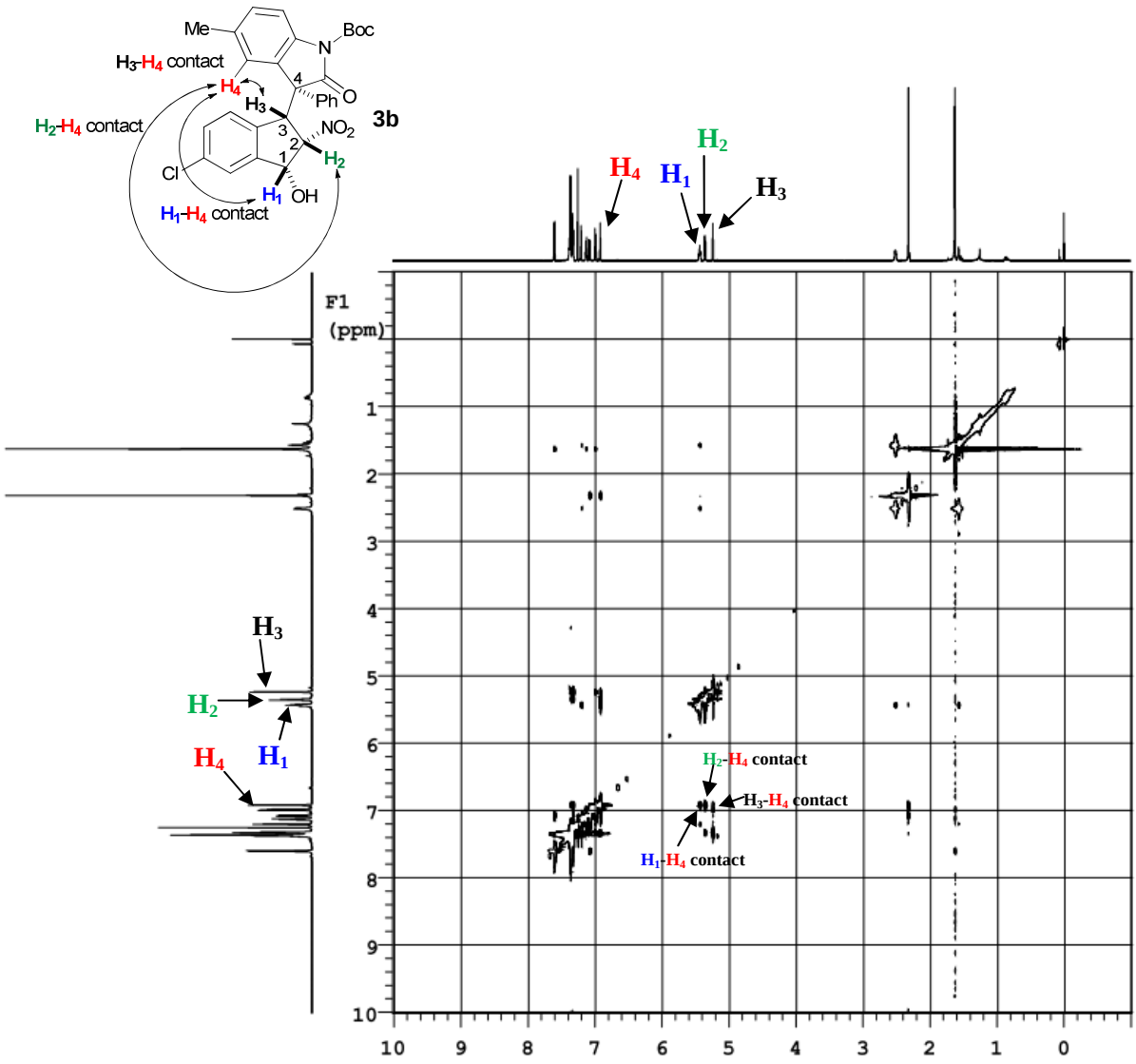
Determination of the relative configuration of 3a and 3b by NOESY and ^{13}C NMR

Only long range NOESY contacts can be reliably used in structure elucidation of five member rings due to ring flexibility. Vicinal NOESY contacts are unreliable in five membered rings in determining *cis*/*trans* spatial positioning.[4,5] Relative configuration of the cascade products were assigned in analogy to long range NOESY contacts from compound **3a** and **3b**.

Long Range NOESY contacts



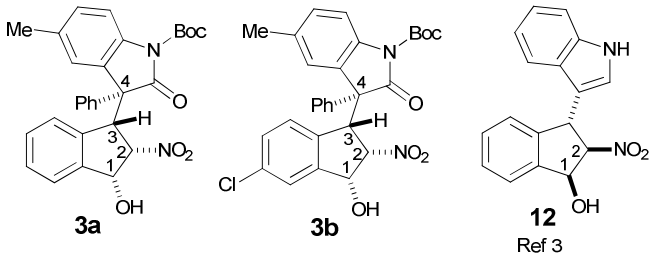
Long Range NOESY contacts



Determination of the relative configuration of 3a and 3b by α,β hydroxyl effects on the ^{13}C NMR shift

The α and β hydroxyl effects on the ^{13}C NMR shifts provide information of *cis*/*trans* relative configuration of the proton on C1 and C2.

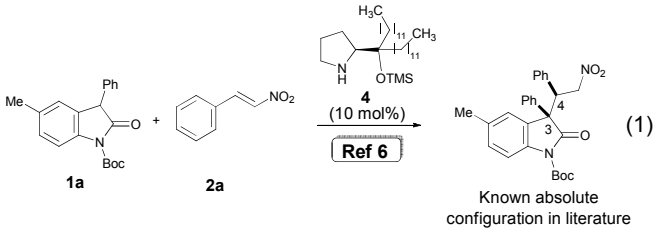
By inspection of the ^{13}C NMR shift of C1 (α-carbon) and C2 (β-carbon) with known literature values, the measured data is consistent with reported values for *cis*-nitroindanols. Therefore, the OH and NO_2 groups are *cis*- positioned, confirming the data obtained from the long range NOESY contacts. [3,5]



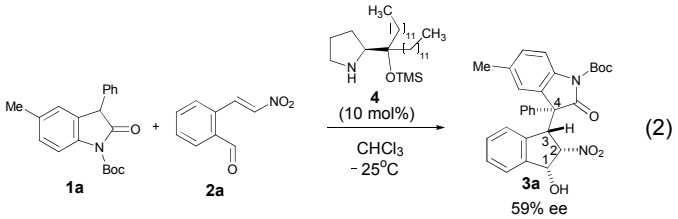
^{13}C NMR shift	C1	C2
Compound **3a**	75.7 ppm	91.9 ppm
Compound **3b**	75.2 ppm	91.9 ppm
Compound **12**	74.8 ppm	94.1 ppm

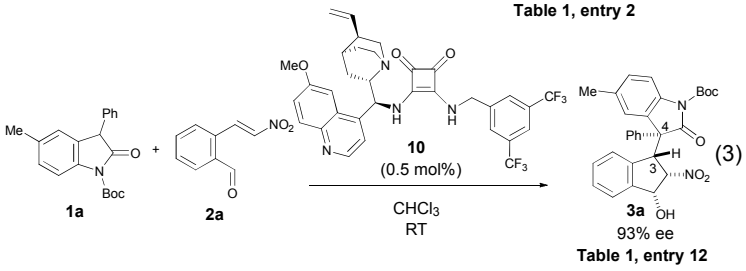
Determination of the absolute configuration by analogy

While efforts were conducted to yield crystals for absolute configuration, no suitable X-ray quality crystals could be obtained through testing a series of solvents and crystallization techiques. Therefore, the absolute configuration of **3a** was determined by analogy of the first Michael addition reaction of this domino reaction to previously reported Michael additions using TMS-protected di-dodecyl prolinol **4** as catalyst (eqn 1, figure below).[6]

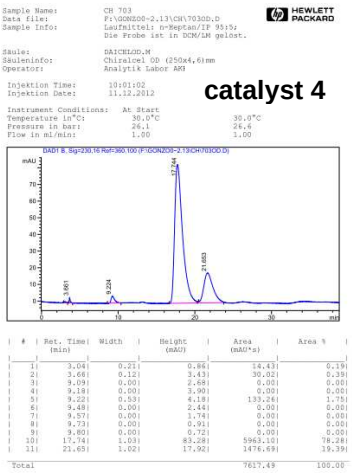


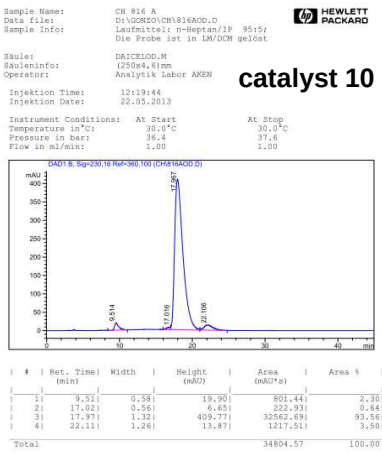
This project - From table 1 (manuscript)



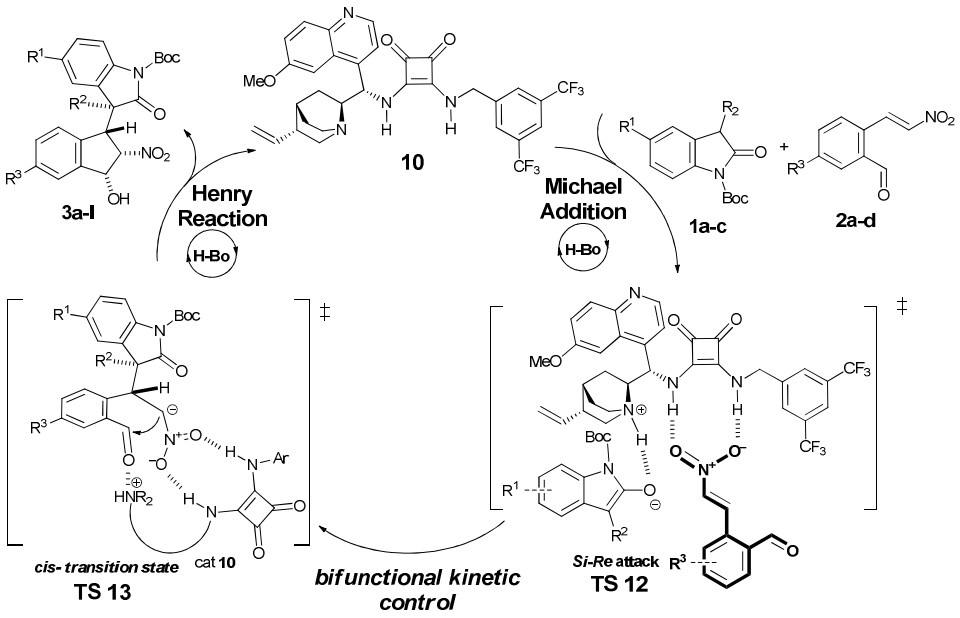


In our catalyst screening (Table 1 in manuscript), the relative topicity is the same for both catalyst **4** and catalyst **10** used in our methodology. Hence catalyst **4** and catalyst **10** generates the same major enantiomer **3a** based on chiral HPLC comparison (see HPLC chromatograms below). With that, the absolute configuration at carbon 3 and carbon 4 (labeled in figure above) of **3a** , can be deduced by analogy to reference 6.





Proposed mechanism for diastereo- and enantiocontrol of the domino reaction



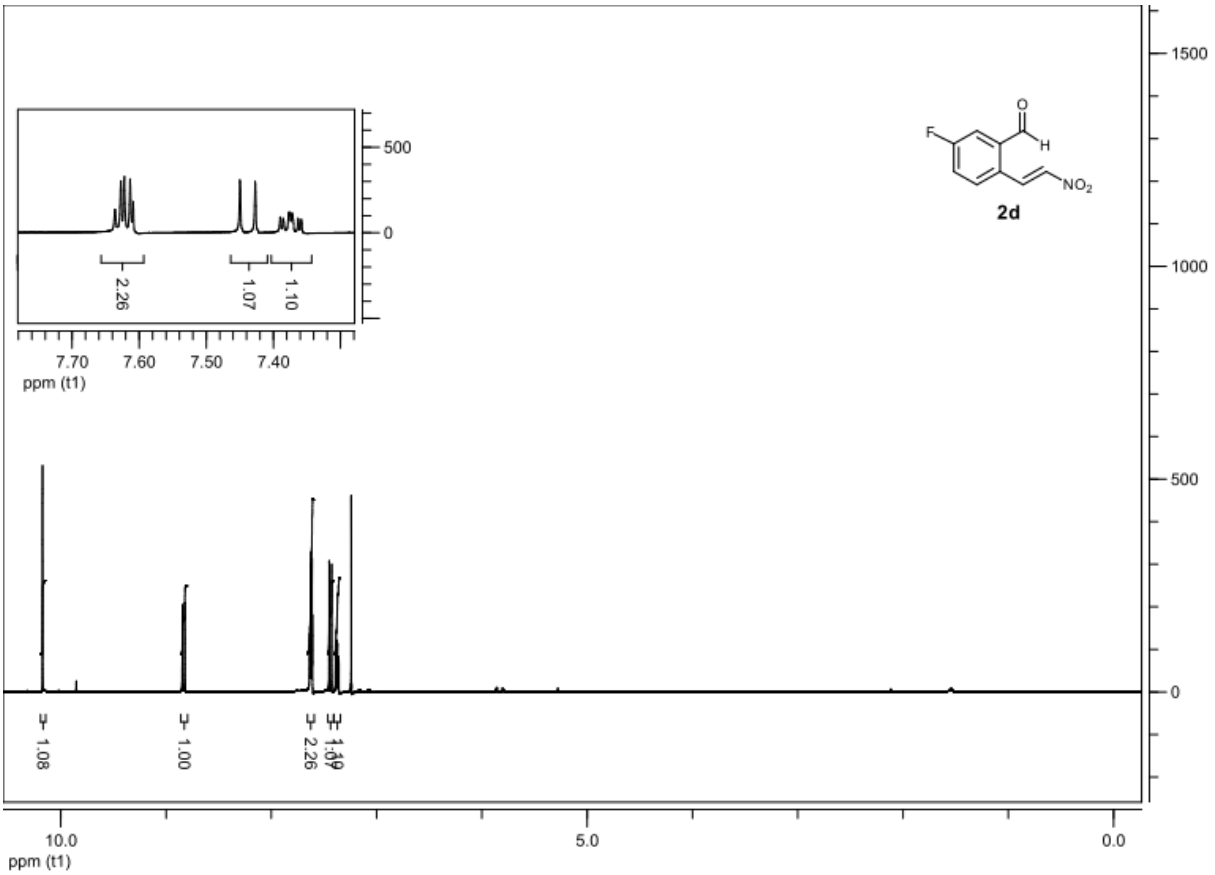
The control of enantio-induction of the cascade product **3a-l** can be attributed to transition state **TS 12** where a *Si-Re* attack occurs between the oxindole **1** and the *o*-carbaldehyde nitroolefin **2** in the hydrogen bonding catalyzed first Michael addition step. The proposed transition state using catalyst **10** is consistent with that suggested by Jørgensen *et. al.* for other Michael additions with the same catalyst.[7]

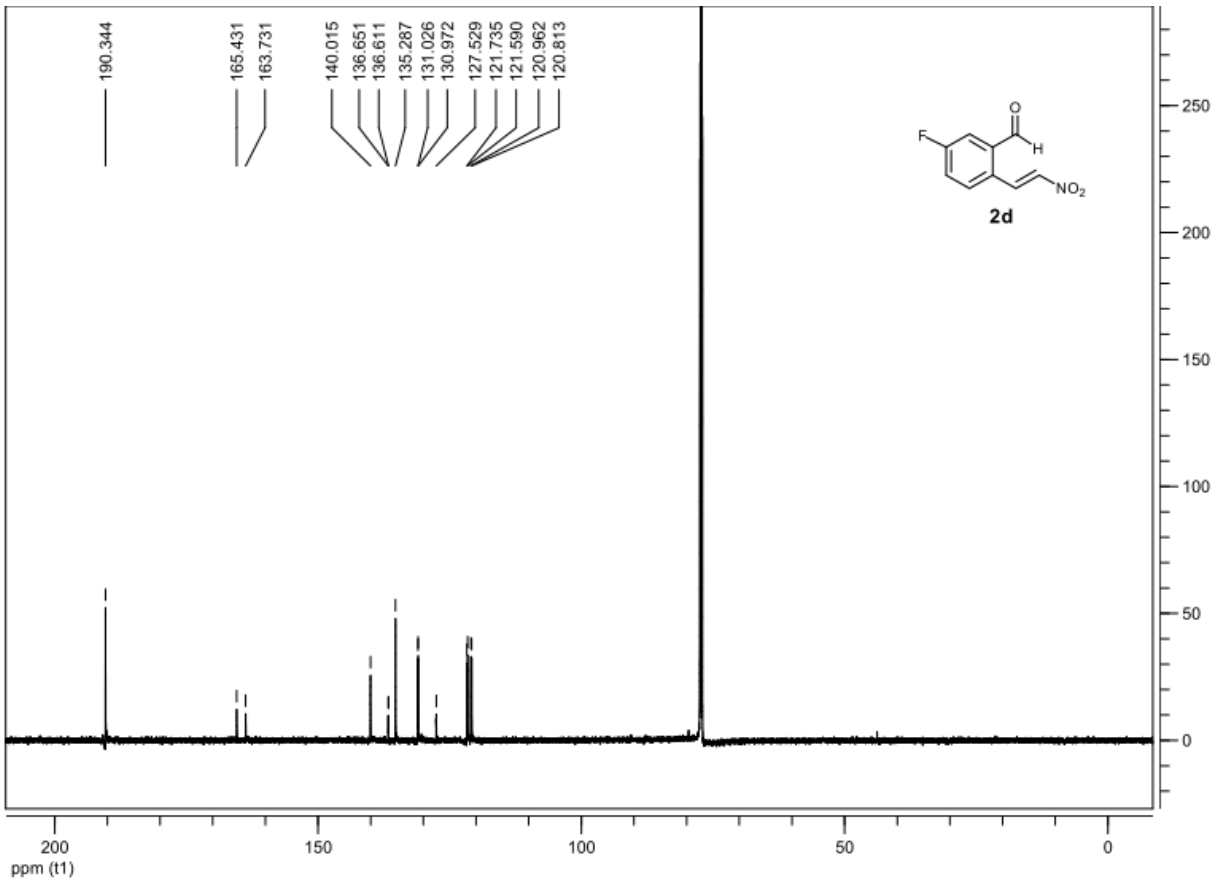
In the second Henry reaction step, our proposed mechanism involved catalyst **10** binding both the nitro group and the aldehyde moiety in a *cis*-positioned transition state **TS13** through bifunctional kinetic control, a concept we previously introduced.[3] The cascade products **3a-l** were then subsequently generated with the nitro-indanol functionalities positioned *cis* relative to each other, and the squaramide catalyst **10** re-enters the catalytic cycle.

Reference

[1] (a) A. Huang, J. Kodanko, L. E. Overman, *J. Am. Chem. Soc.* 2004, **126**, 14043; (b) T. Ishimaru, N. Shibata, J. Nagai, S. Nakamura, T. Toru, S. Kanemasa, *J. Am. Chem. Soc.* 2006, **128**, 16488; (c) S-W. Duan, J. An, J-R. Chen, W-J. Xiao *Org. Lett.* 2011, **13**, 2290.
[2] M. Asami, A. Taketoshi, K. Miyoshi, H. Hoshino, K. Sakakibara, *Chem. Lett.* 2007, **36**, 64.
[3] C. C. J. Loh, I. Atodiresei, D. Enders, *Chem. Eur. J.* 2013, **19**, 10822.
[4] J. G. Napolitano, J. A. Gávin, C. Gárcia, M. Norte, J. J. Fernández, A. H. Daranas, *Chem. Eur. J.* 2011, **17**, 6338.
[5] S. Quideau, J. Ralph, *J. Chem. Soc. Perkin. Trans. I* 1993, 653.
[6] C. Wang, X. Yang, D. Enders, *Chem. Eur. J.* 2012, **18**, 4832.
[7] H. Jiang, M. W. Paixão, D. Monge, K. A. Jørgensen, *J. Am. Chem. Soc.* 2010, **132**, 2775.

NMR Spectra


2.26
1.07
1.10
7.70
7.60
7.50
7.40
ppm (t1)
1.08
1.00
2.26
1.09
10.0
5.0
0.0
ppm (t1)
2d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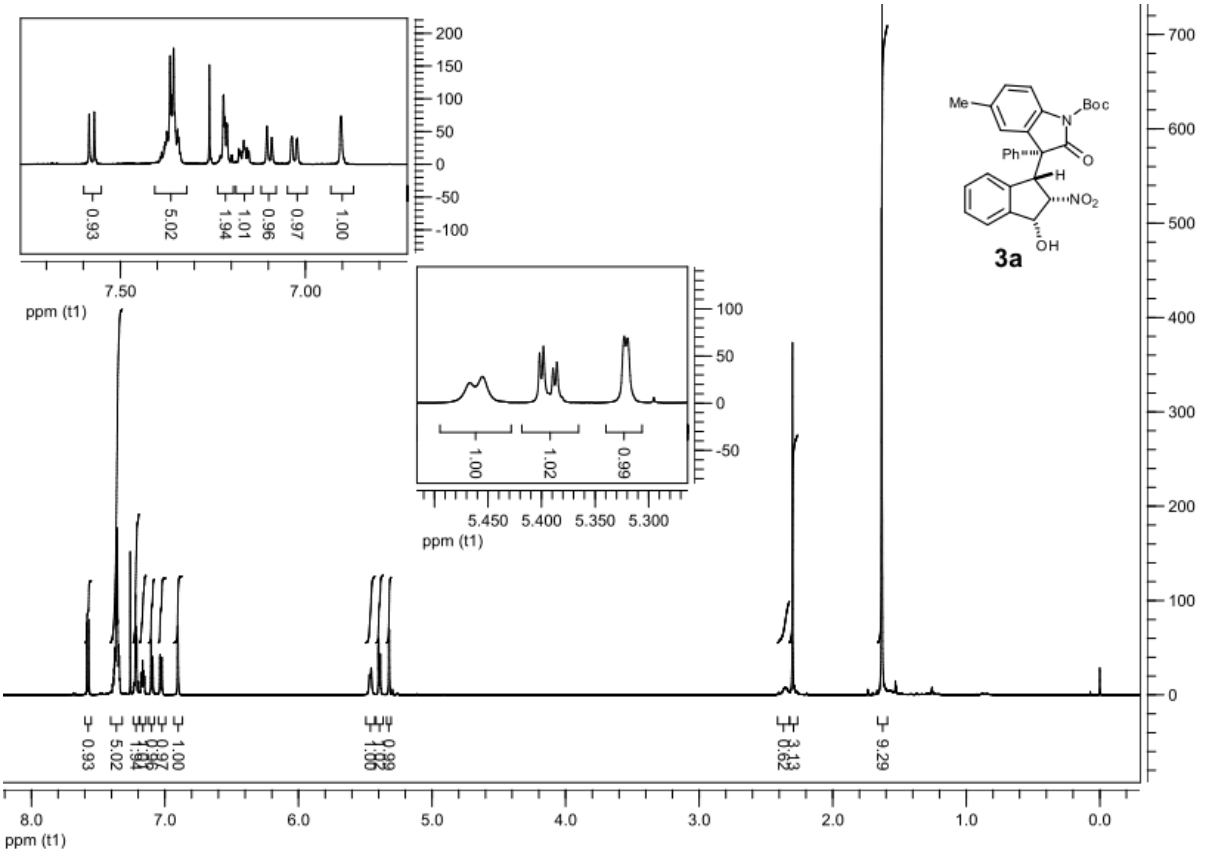
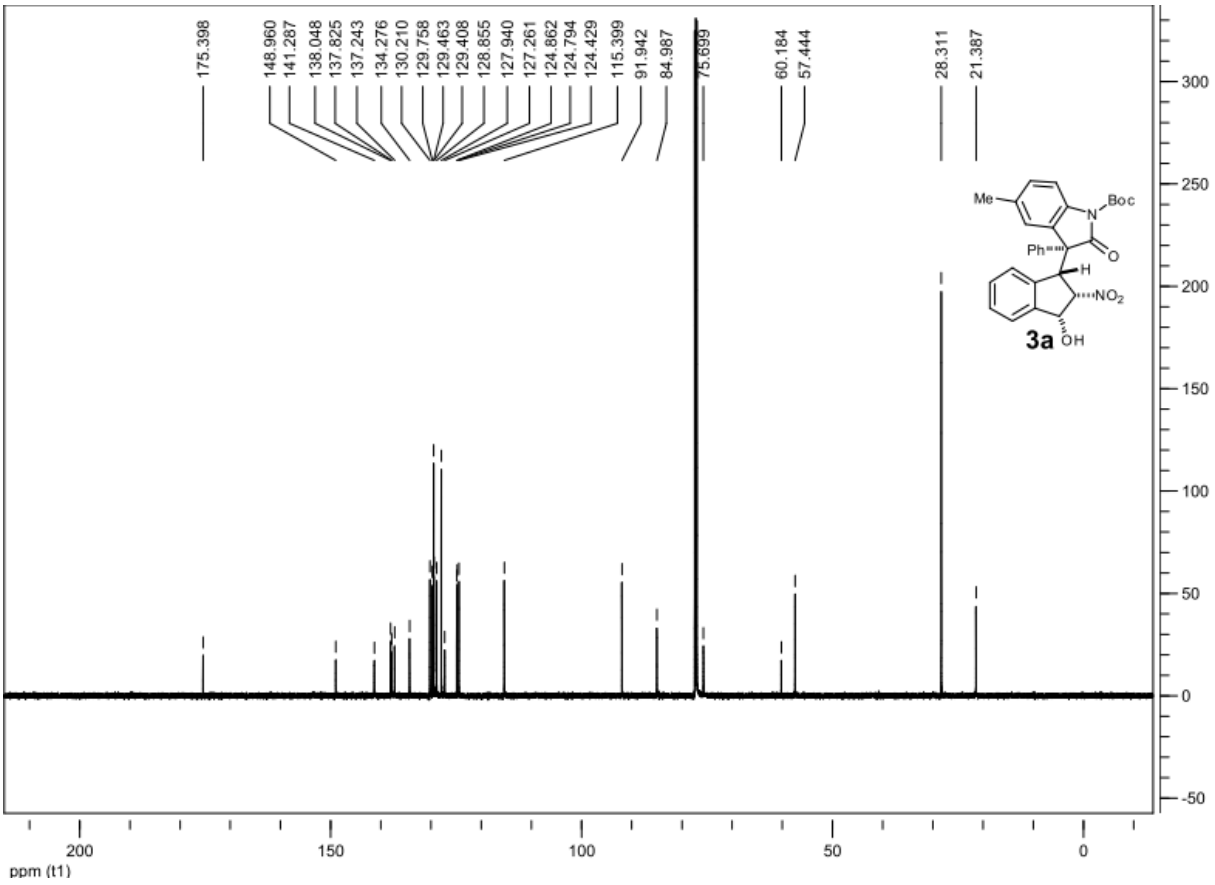
165.431
163.731
140.015
136.651
136.611
135.287
131.026
130.972
127.529
121.735
121.590
120.962
120.813
200
150
100
50
0
ppm (t1)
2d


Me
Boc
N
Ph
O
H
NO2
OH
3a
ppm (t1)
0.93
5.02
1.94
1.01
0.96
0.97
1.00
1.00
1.02
0.99
2.13
9.29


175.398
148.960
141.287
138.048
137.825
137.243
134.276
130.210
129.758
129.463
129.408
128.855
127.940
127.261
124.862
124.794
124.429
115.399
91.942
84.987
75.699
60.184
57.444
28.311
21.387
Me
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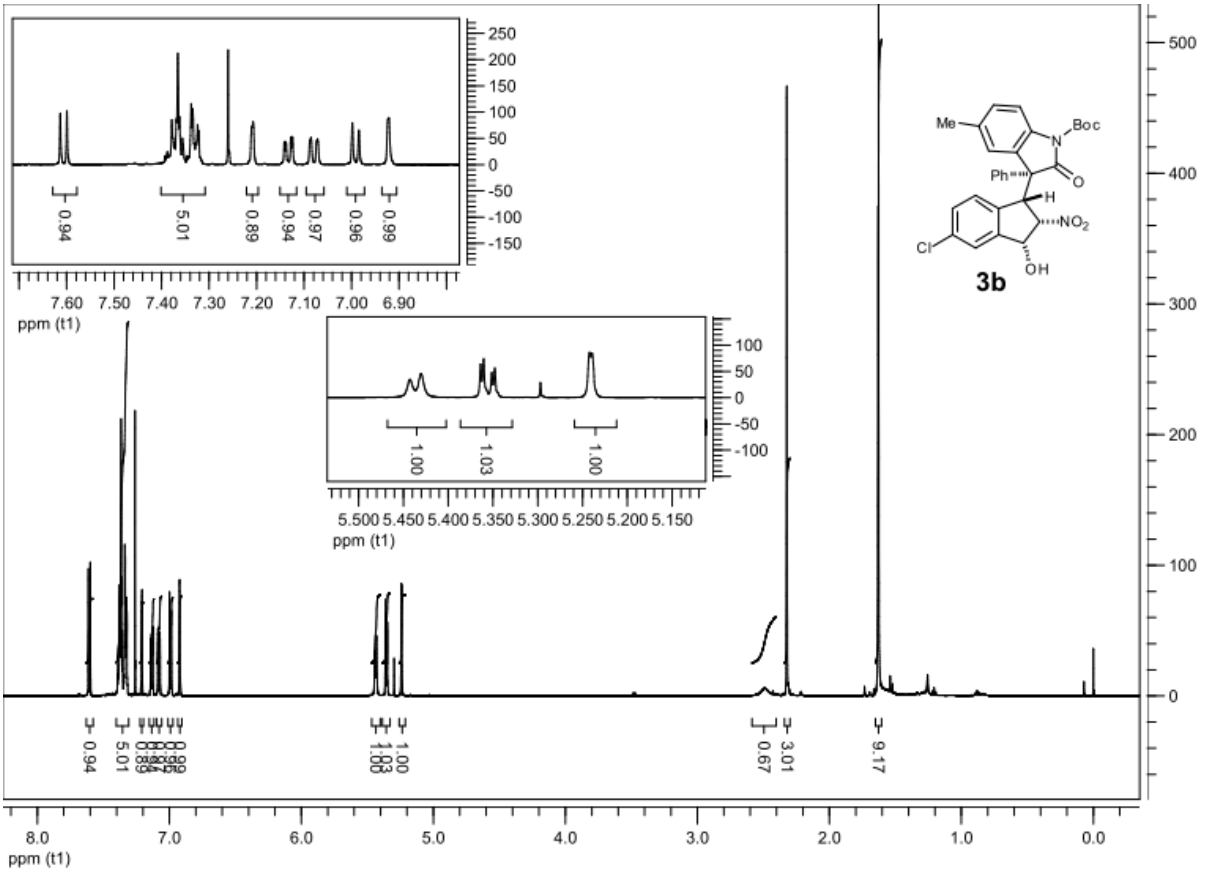
N
Ph
O
H
NO2
OH
3a
ppm (t1)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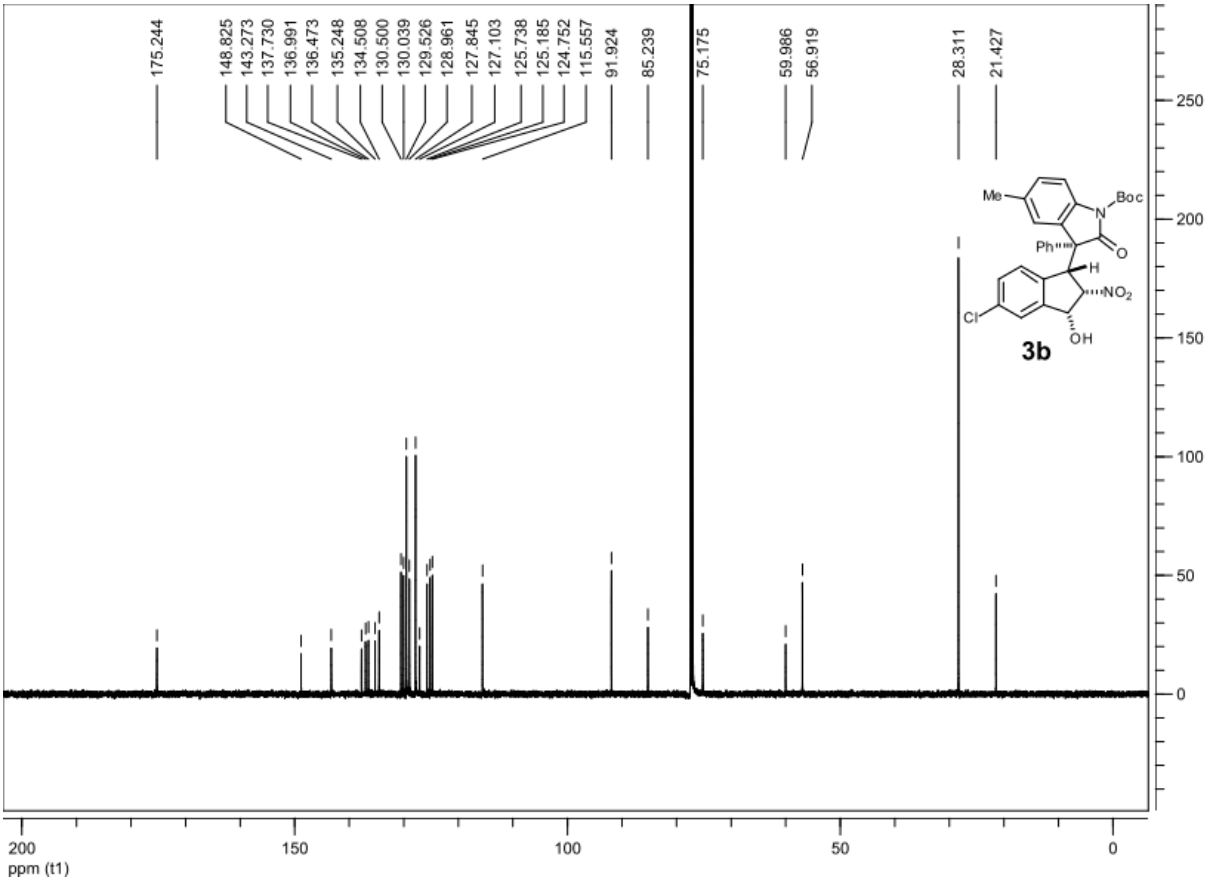
5.01
0.89
0.94
0.97
0.96
0.99
7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90
ppm (t1)
1.00
1.03
1.00
5.500 5.450 5.400 5.350 5.300 5.250 5.200 5.150
ppm (t1)
0.94
5.01
1.08
1.00
0.67
3.01
9.17
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)
Me
Boc
N
Ph
O
H
NO2
Cl
OH
3b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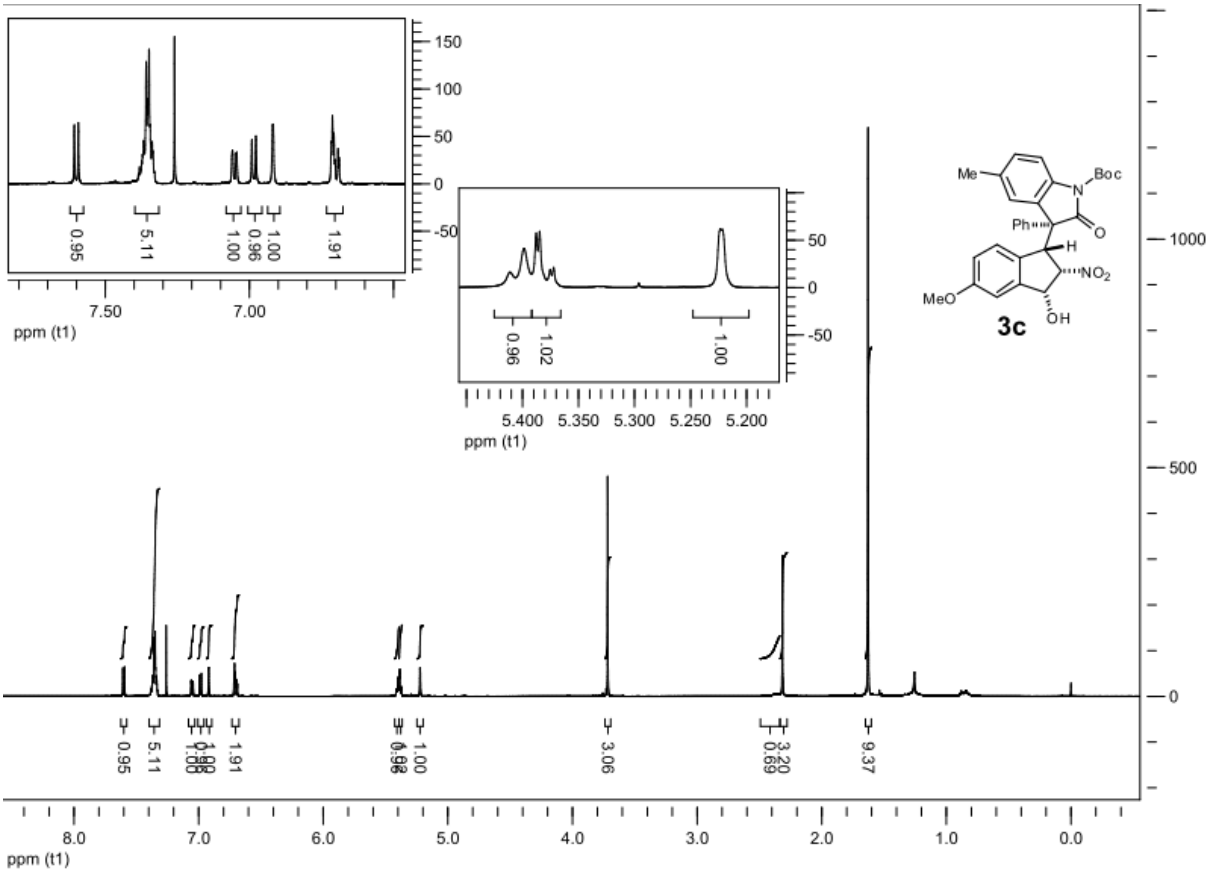
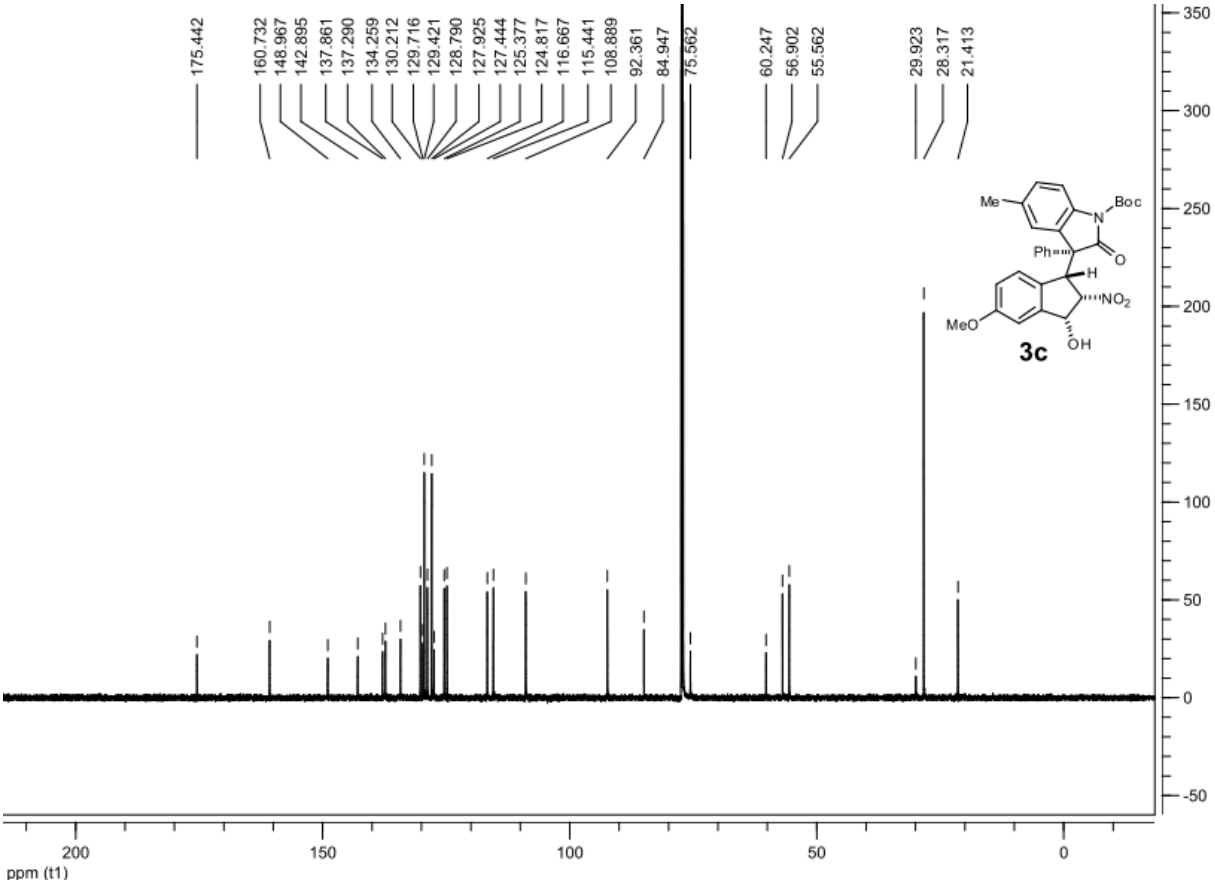
148.825
143.273
137.730
136.991
136.473
135.248
134.508
130.500
130.039
129.526
128.961
127.845
127.103
125.738
125.185
124.752
115.557
91.924
85.239
75.175
59.986
56.919
28.311
21.427
200 150 100 50 0
ppm (t1)
Me
Boc
N
Ph
O
H
NO2
Cl
OH
3b


Me
Boc
N
Ph
O
H
NO2
MeO
OH
3c
ppm (t1)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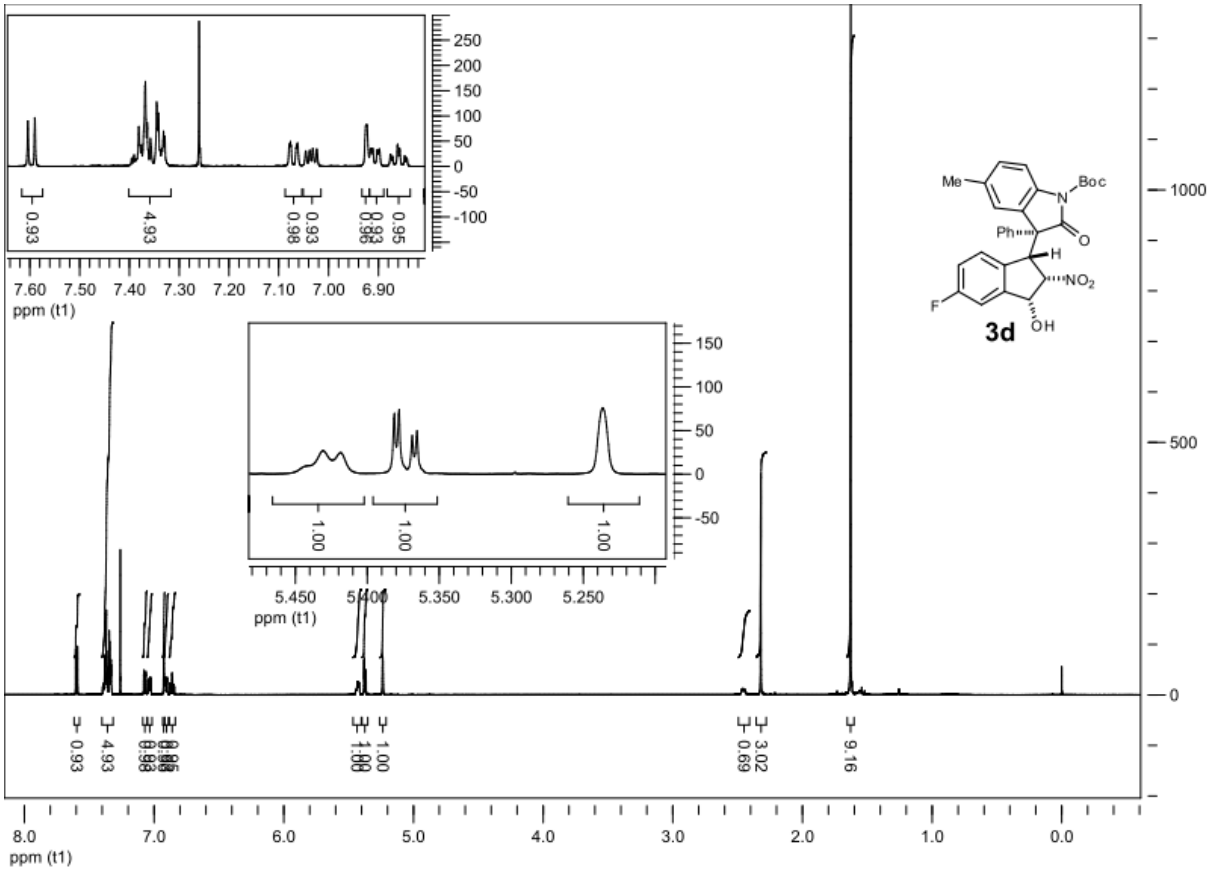
160.732
148.967
142.895
137.861
137.290
134.259
130.212
129.716
129.421
128.790
127.925
127.444
125.377
124.817
116.667
115.441
108.889
92.361
84.947
75.562
60.247
56.902
55.562
29.923
28.317
21.413
Me
Boc
N
Ph
O
H
NO2
MeO
OH
3c
ppm (t1)


Me
Boc
N
Ph
O
H
NO2
F
OH
3d
ppm (t1)
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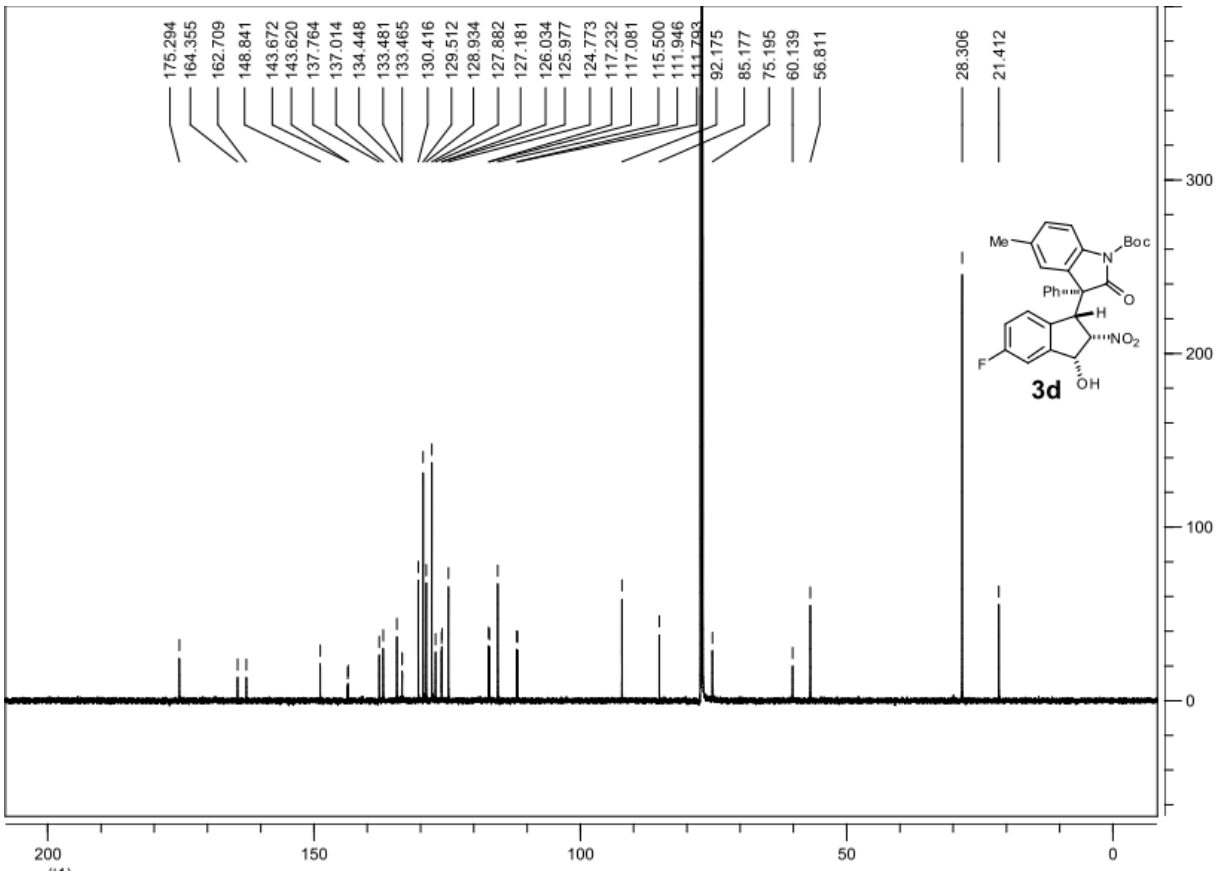
4.93
0.98
0.93
0.98
0.95
1.00
1.00
1.00
0.69
3.02
9.16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143.672
143.620
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129.512
128.934
127.882
127.181
126.034
125.977
124.773
117.232
117.081
115.500
111.946
111.793
92.175
85.177
75.195
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56.811
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21.412
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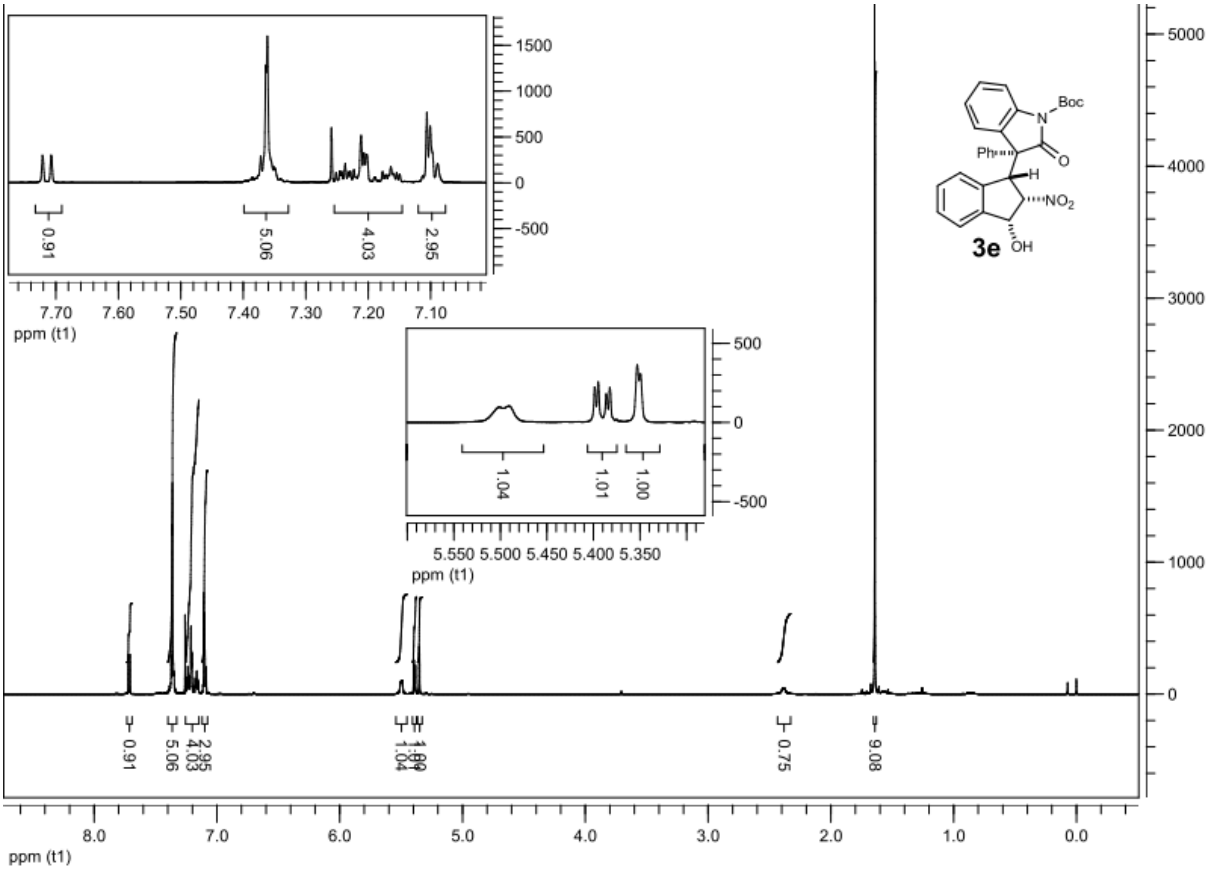
Boc
N
Ph
O
H
NO2
F
OH
3d


3e
Boc
Ph
H
NO2
OH
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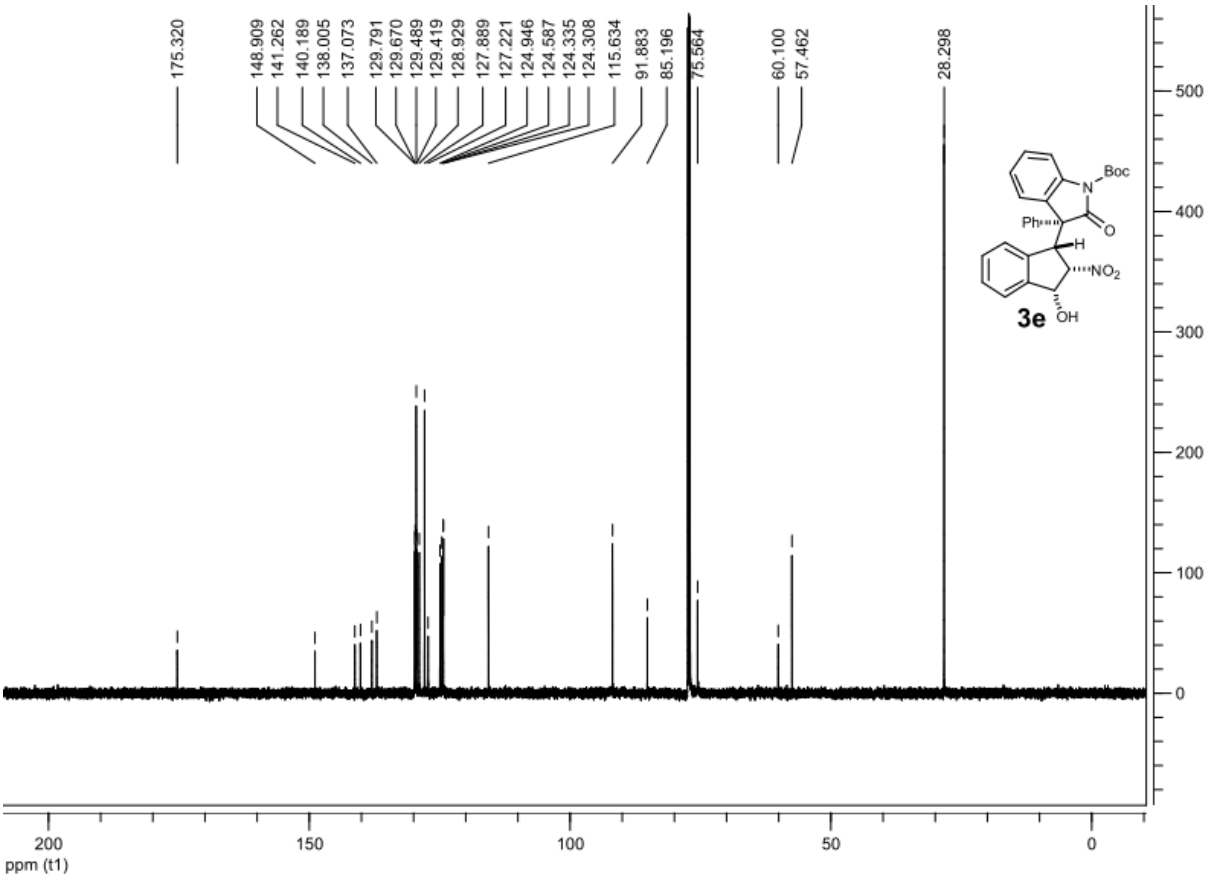
4.03
2.95
1.04
1.01
1.00
0.75
9.08


175.320
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138.005
137.073
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129.670
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127.889
127.221
124.946
124.587
124.335
124.308
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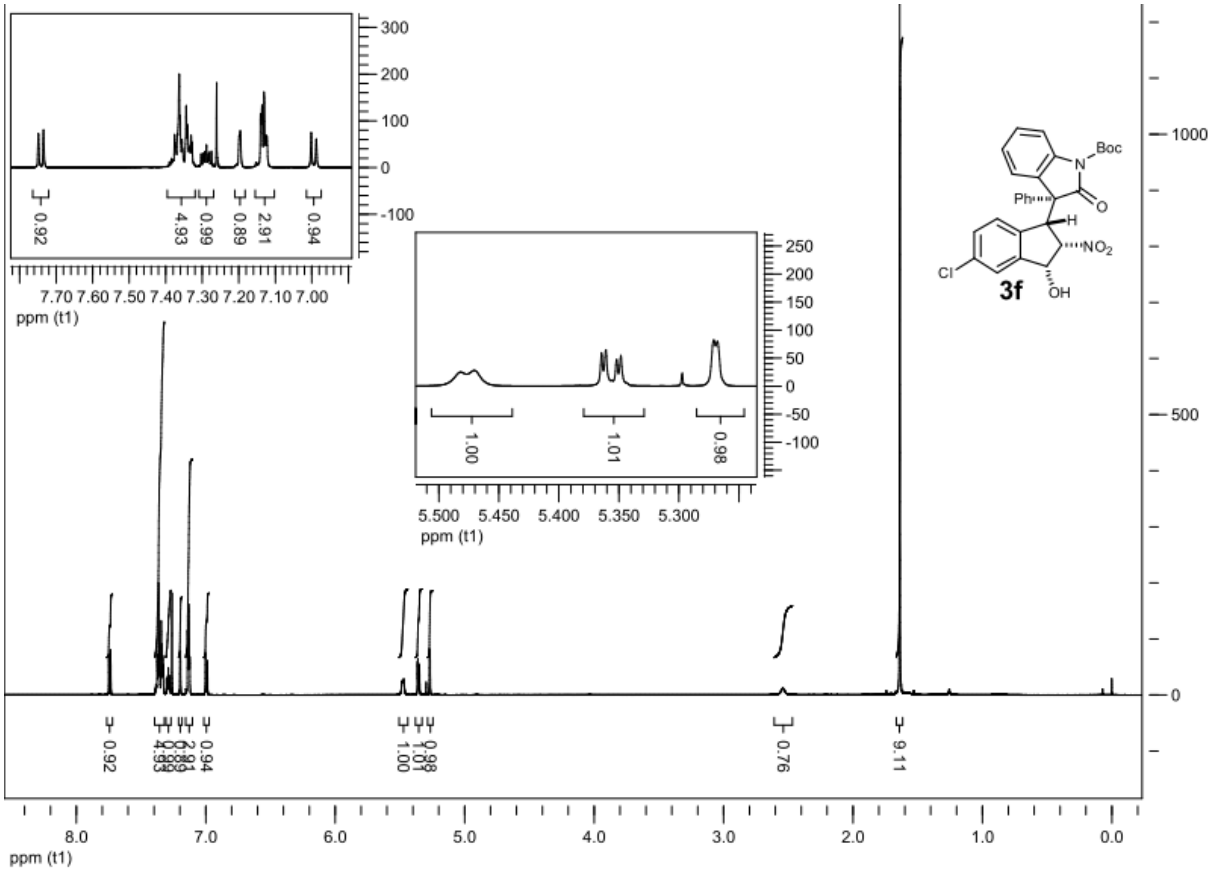
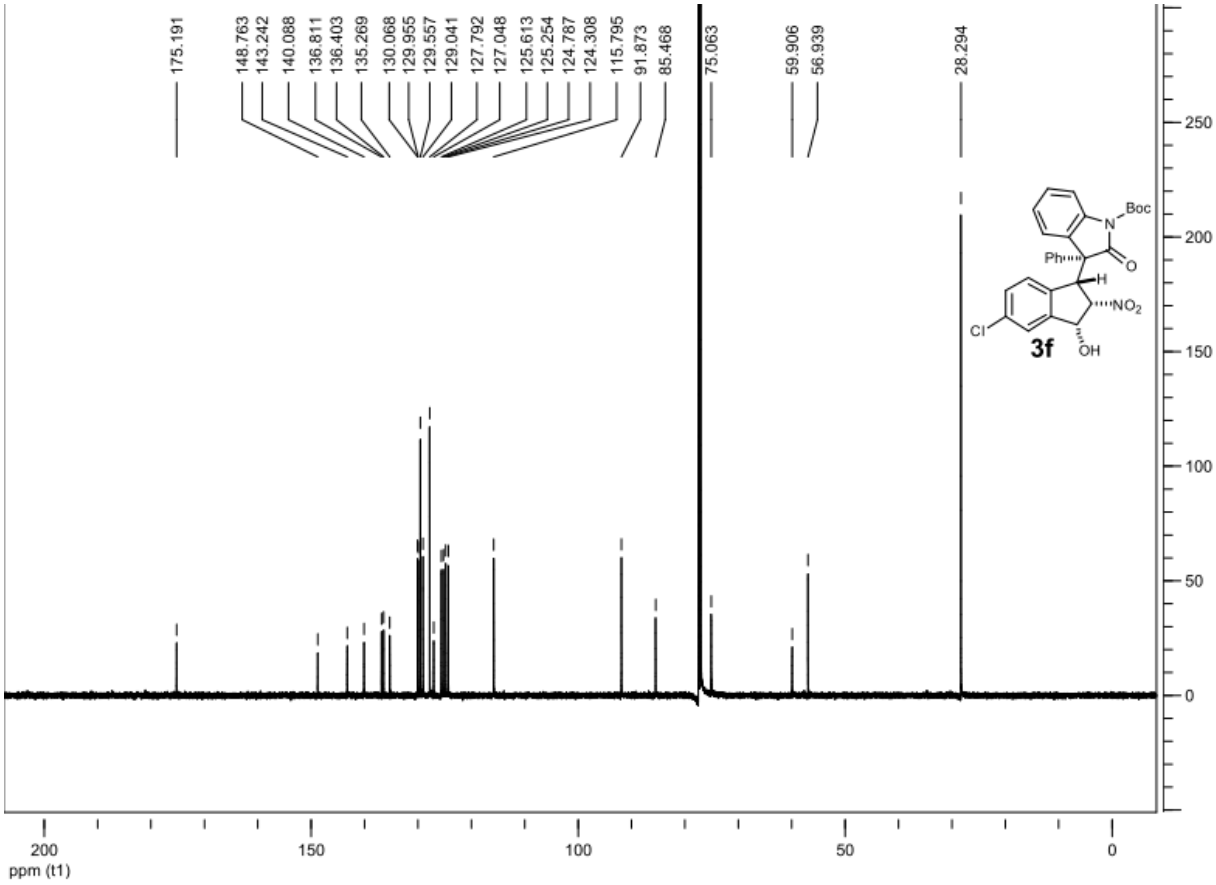
28.298
3e
Boc
Ph
H
NO2
OH
ppm (t1)


0.92
4.93
0.99
0.89
2.91
0.94
7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00
ppm (t1)
1.00
1.01
0.98
5.500 5.450 5.400 5.350 5.300
ppm (t1)
Boc
Ph
H
NO2
Cl
OH
3f
0.92
0.94
1.00
0.98
0.76
6.11
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)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127.048
125.613
125.254
124.787
124.308
115.795
91.873
85.468
75.063
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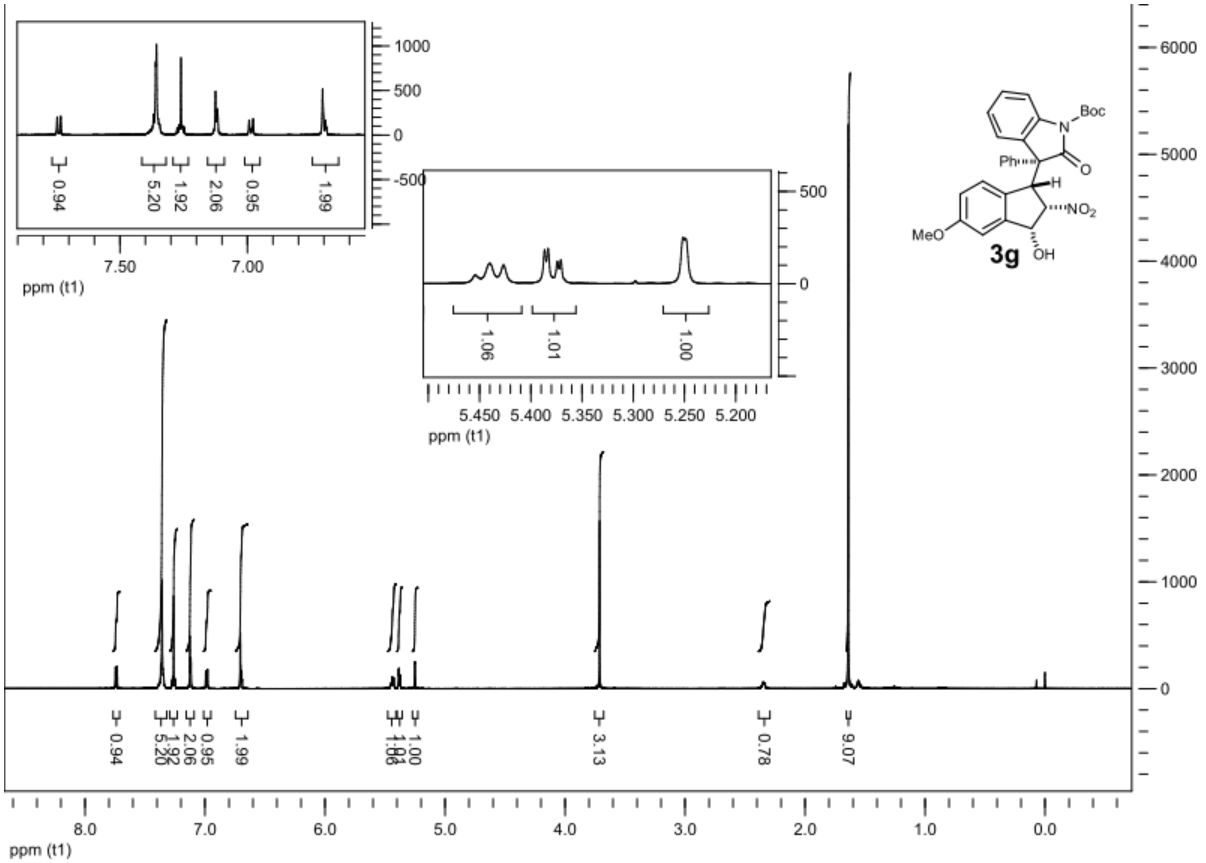
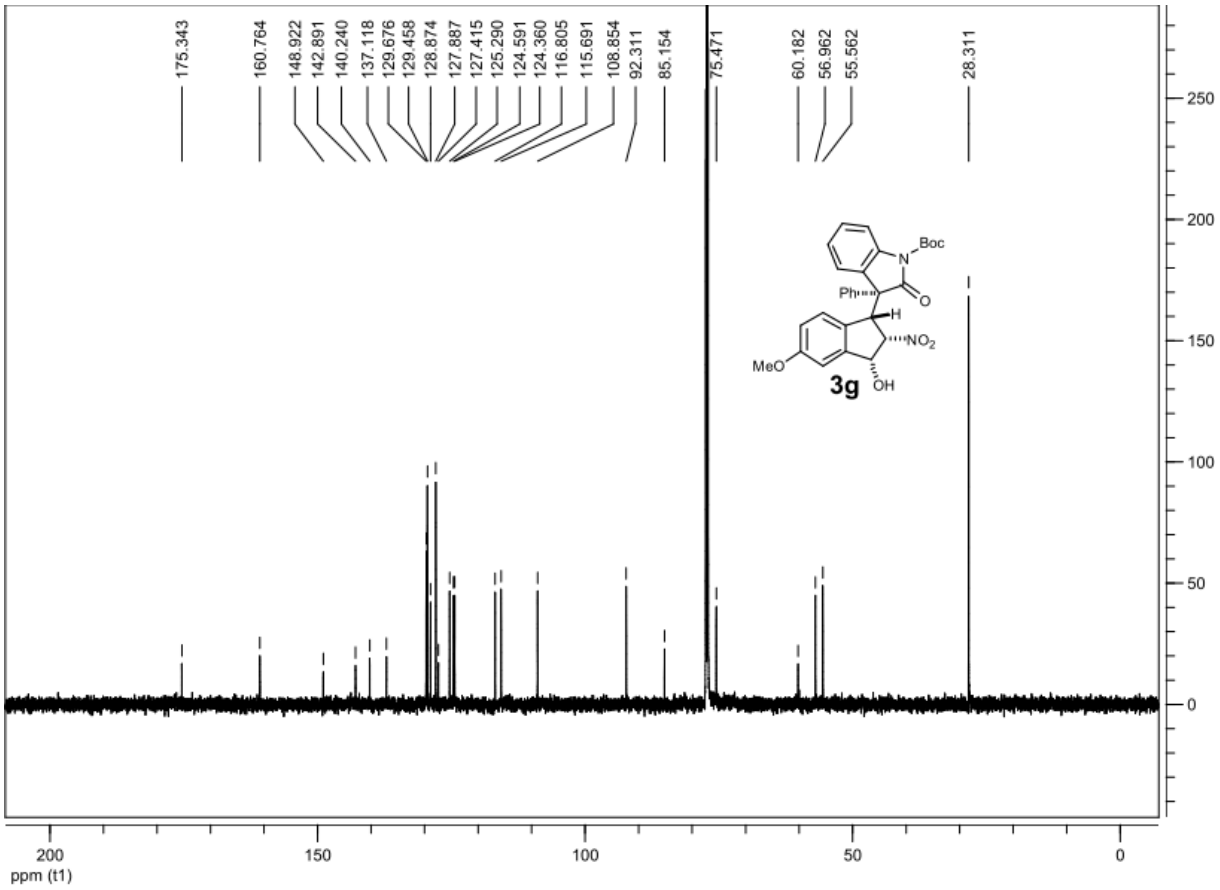
56.939
28.294
Boc
Ph
H
NO2
Cl
OH
3f
200 150 100 50 0
ppm (t1)


0.94
5.20
1.92
2.06
0.95
1.99
7.50
7.00
ppm (t1)
1.06
1.01
1.00
5.450 5.400 5.350 5.300 5.250 5.200
ppm (t1)
Boc
Ph
H
NO2
MeO
OH
3g
0.64
5.20
1.92
2.06
0.95
1.99
1.00
3.13
0.78
9.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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127.887
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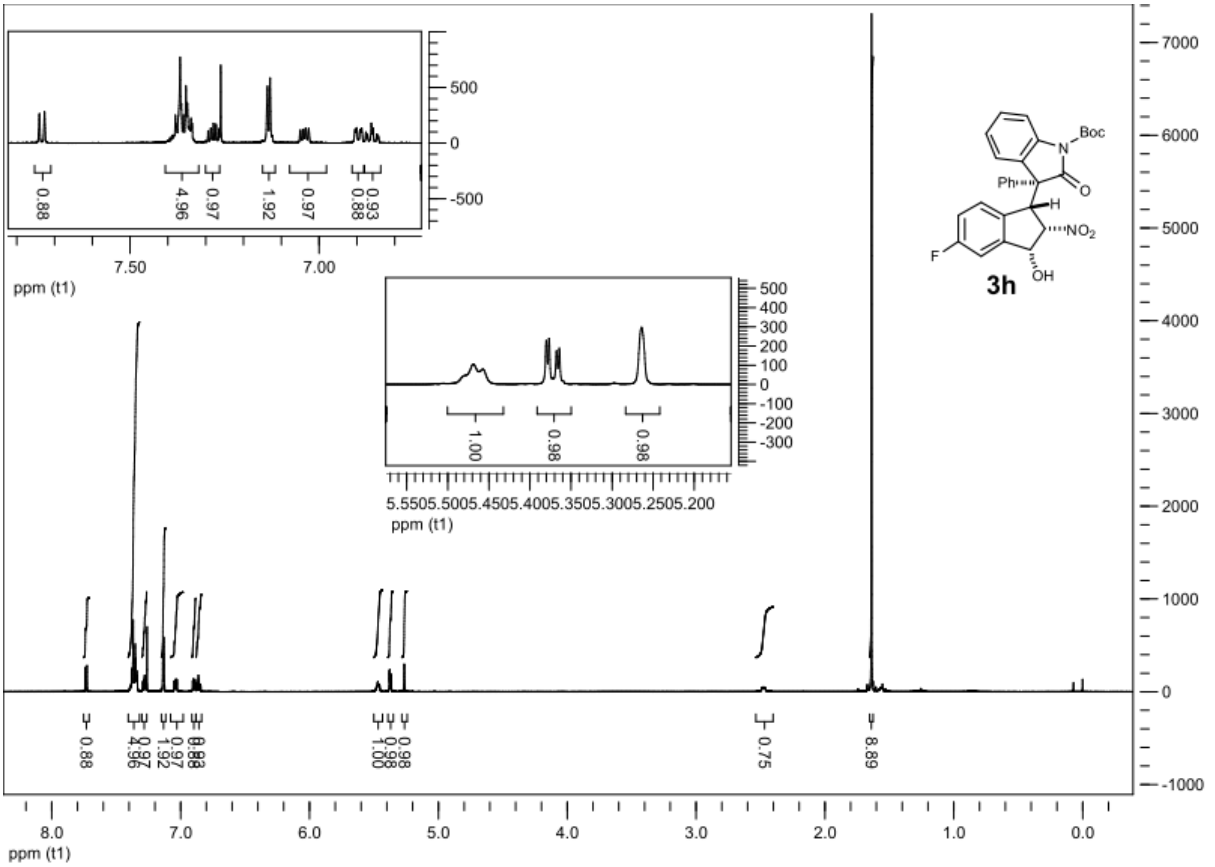
125.290
124.591
124.360
116.805
115.691
108.854
92.311
85.154
75.471
60.182
56.962
55.562
28.311
Boc
Ph
H
NO2
MeO
OH
3g
200
150
100
50
0
ppm (t1)


3h
ppm (t1)
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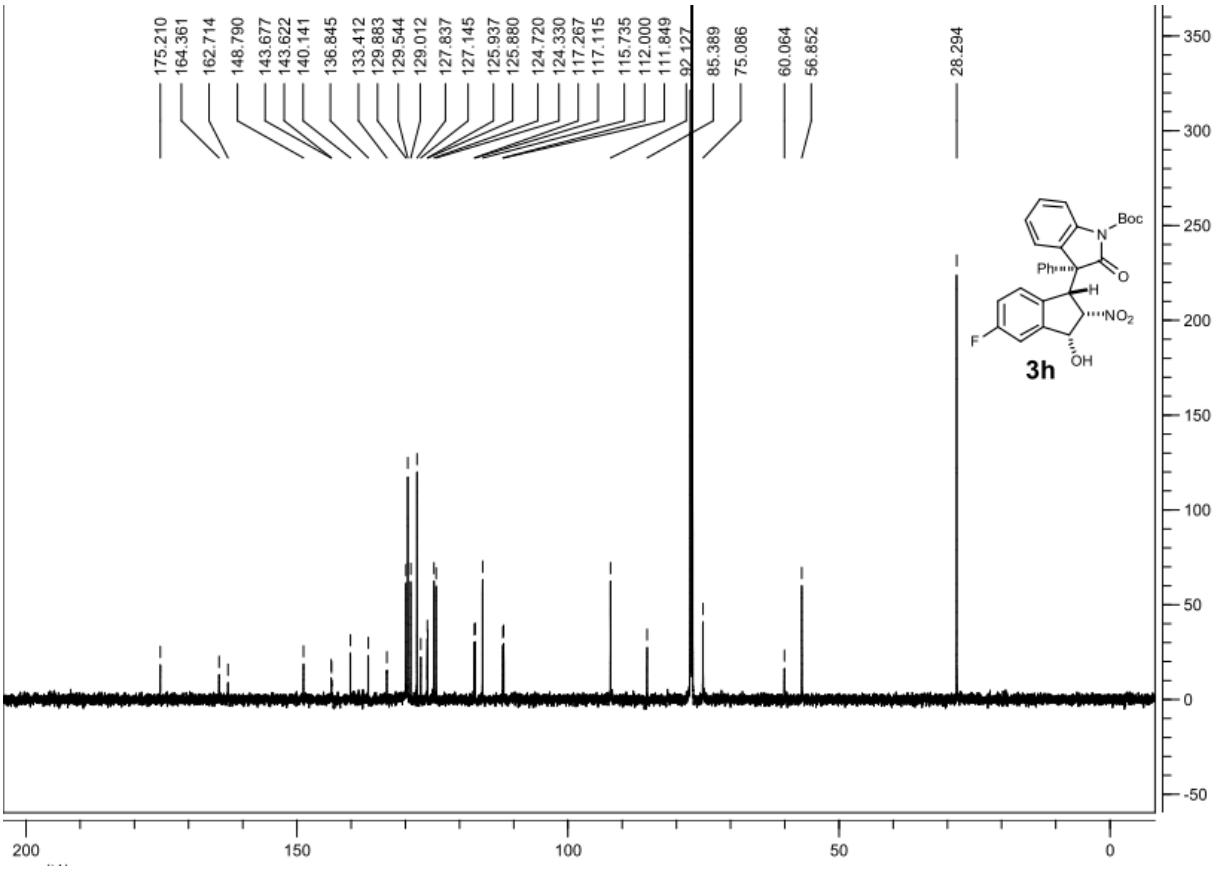
0.97
1.92
0.97
0.88
0.93
1.00
0.98
0.98
0.75
8.89


3h
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143.622
140.141
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133.412
129.883
129.544
129.012
127.837
127.145
125.937
125.880
124.720
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115.735
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60.064
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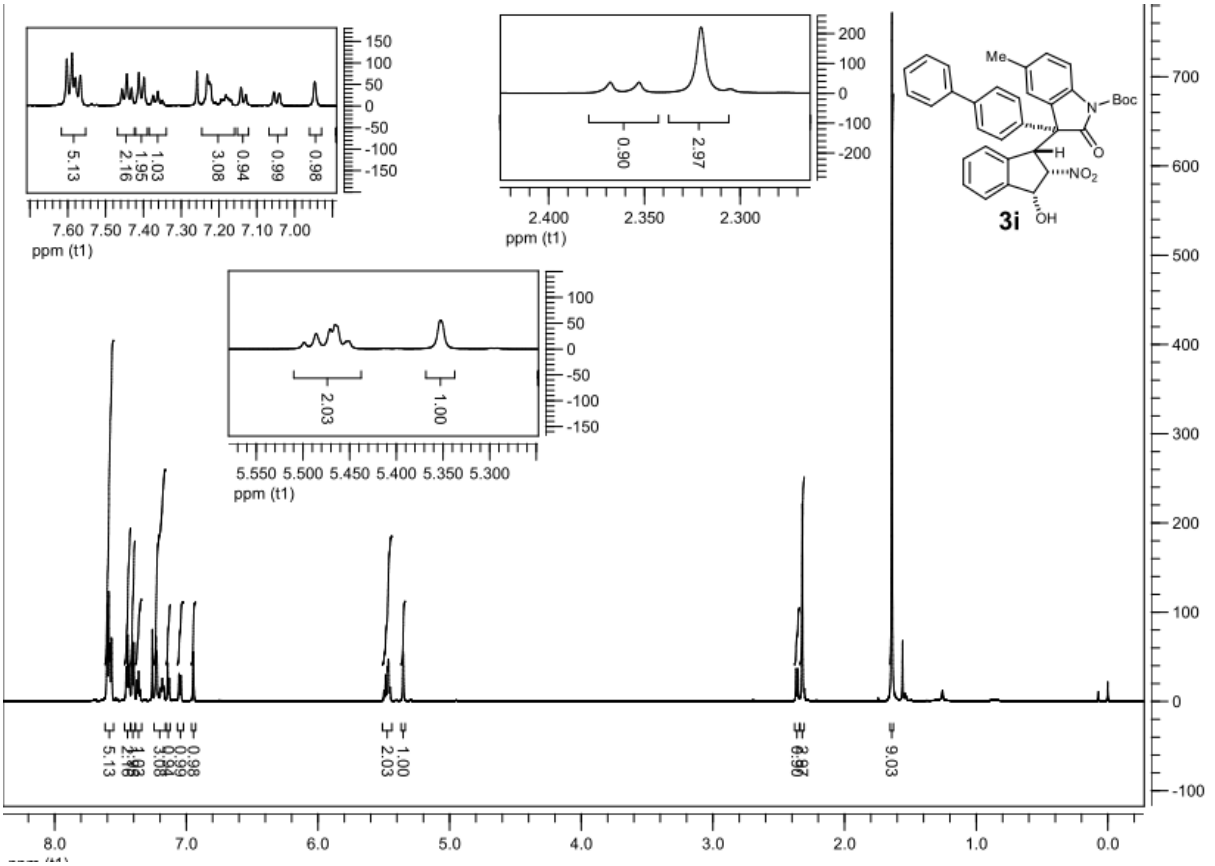
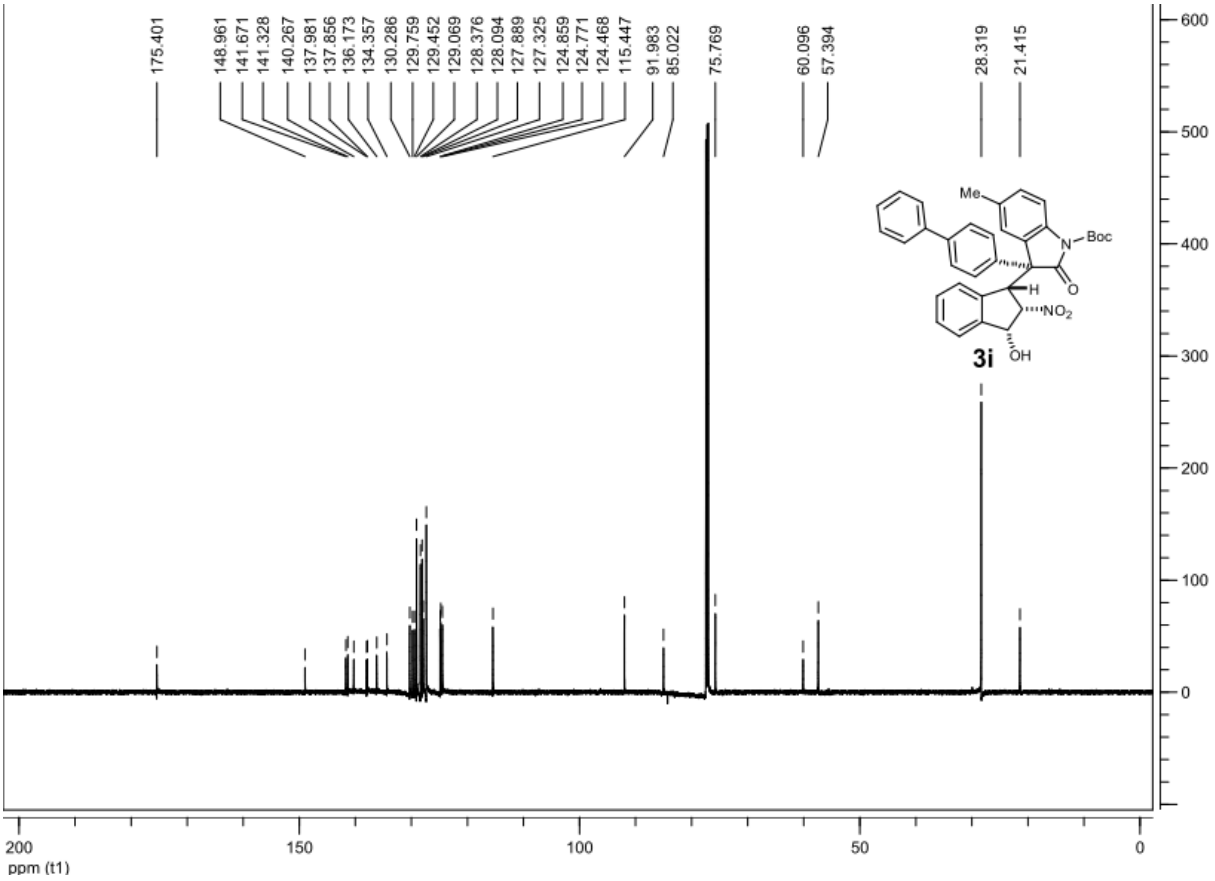
28.294


Me
N
Boc
O
H
NO2
OH
3i
ppm (t1)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136.173
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129.452
129.069
128.376
128.094
127.889
127.325
124.859
124.771
124.468
115.447
91.983
85.022
75.769
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57.394
28.319
21.415
Me
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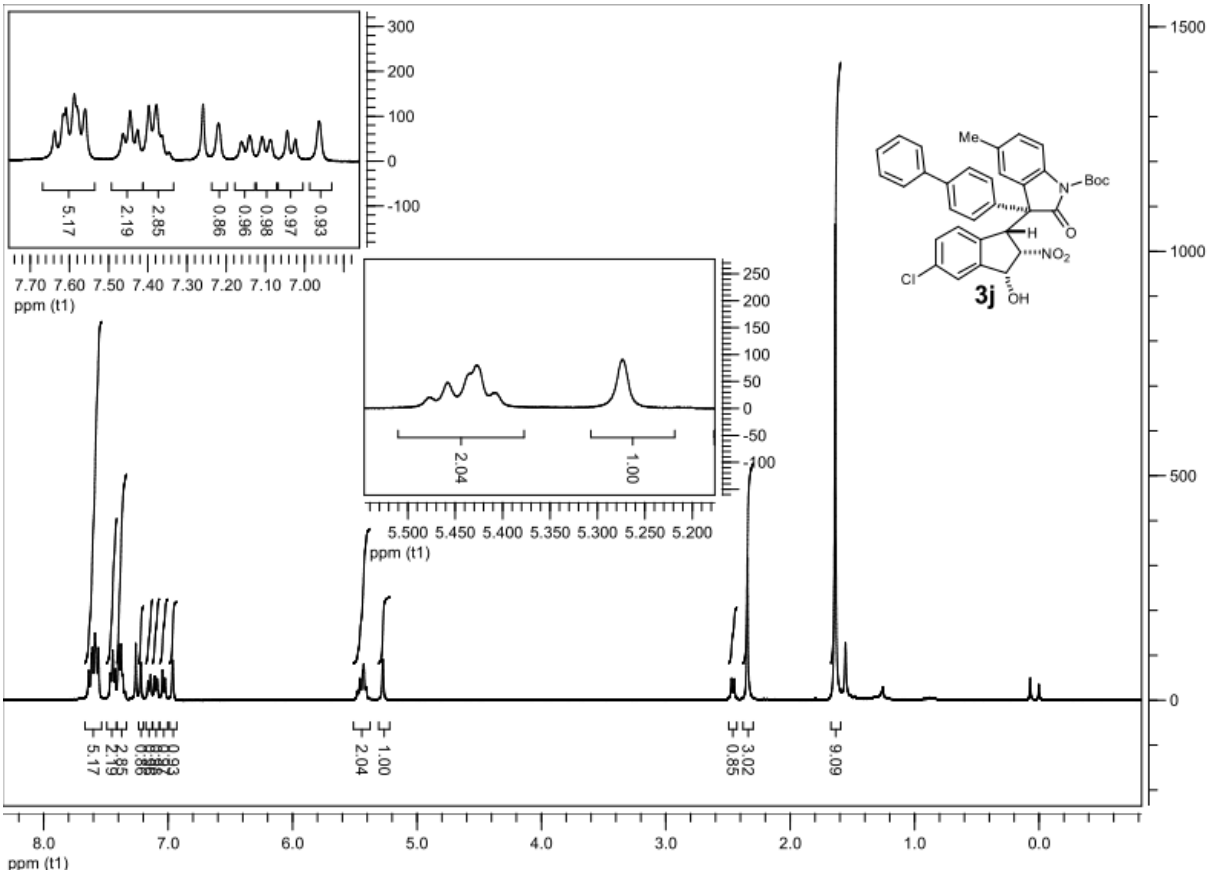
Boc
O
H
NO2
OH
3i
ppm (t1)


Me
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Boc
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H
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Cl
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3j
5.17
2.19
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0.86
0.96
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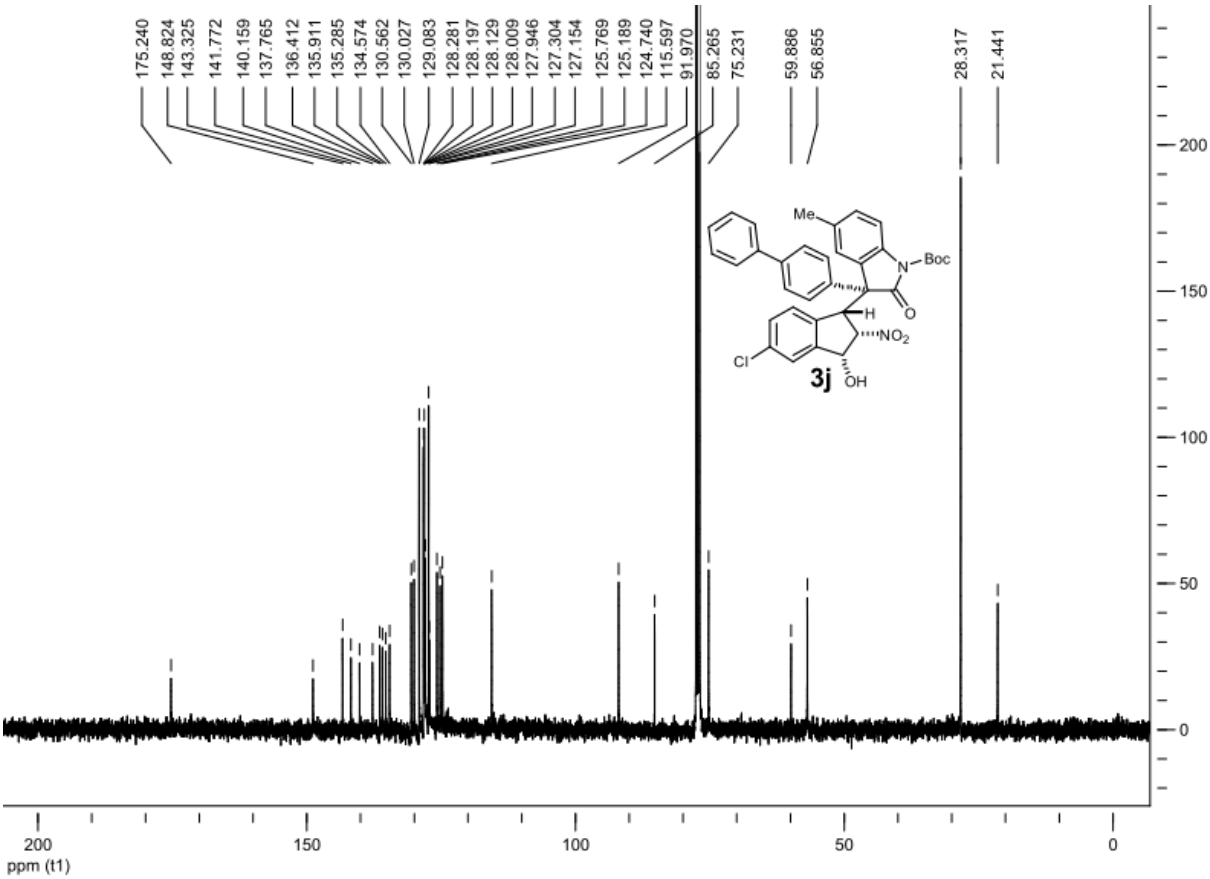
0.97
0.93
2.04
1.00
3.02
9.09
ppm (t1)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140.159
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134.574
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130.027
129.083
128.281
128.197
128.129
128.009
127.946
127.304
127.154
125.769
125.189
124.740
115.597
91.970
85.265
75.231
59.886
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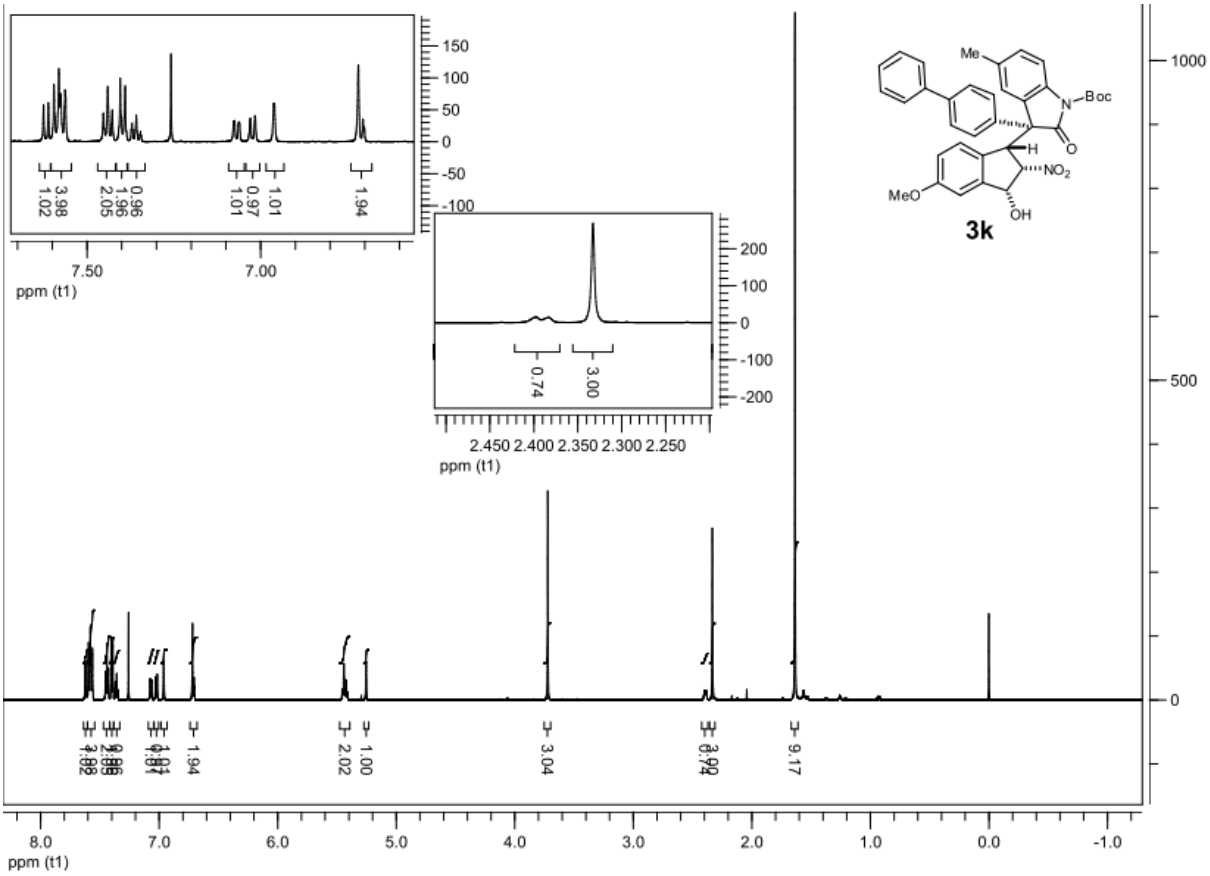
O
H
NO2
Cl
OH
3j
ppm (t1)


Me
N
Boc
O
H
NO2
MeO
OH
3k
ppm (t1)
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7.0
6.0
5.0
4.0
3.0
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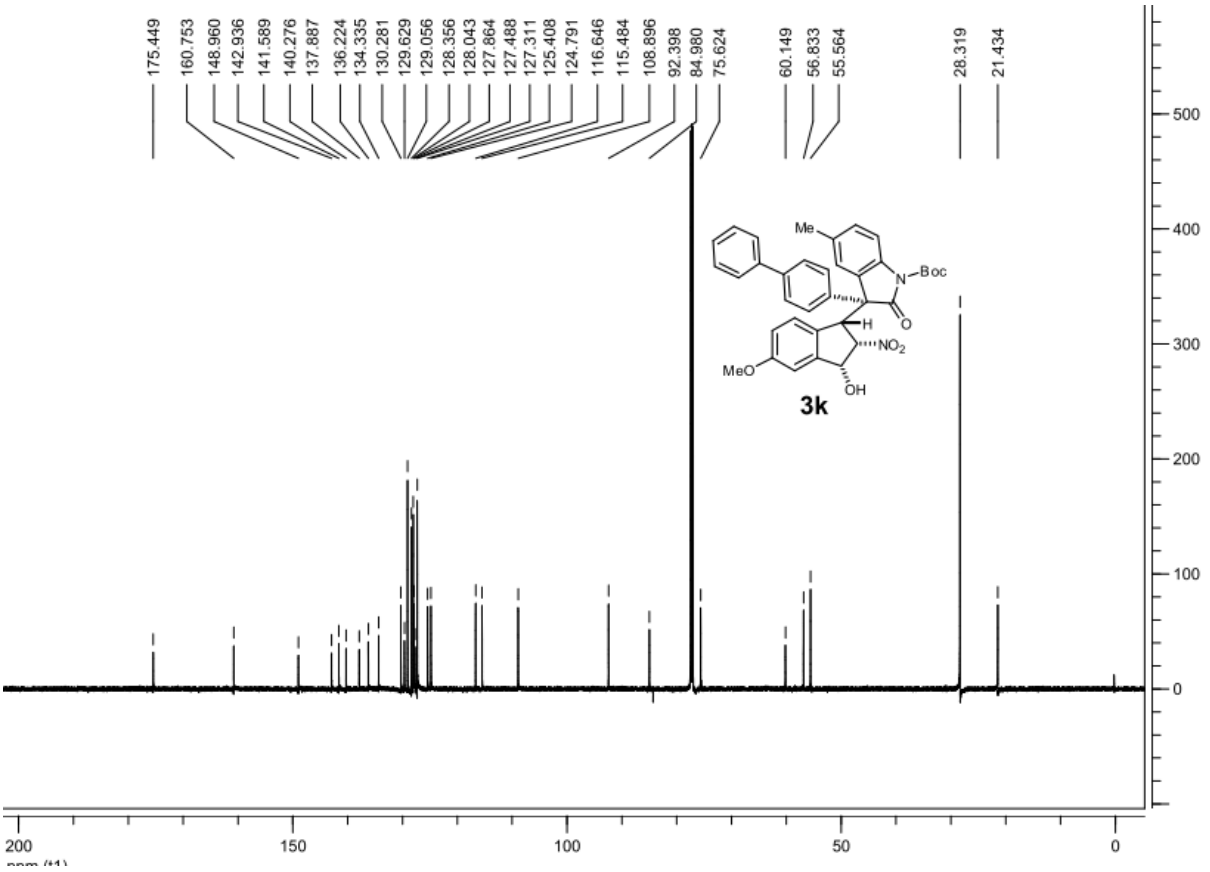
1.0
0.0
-1.0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140.276
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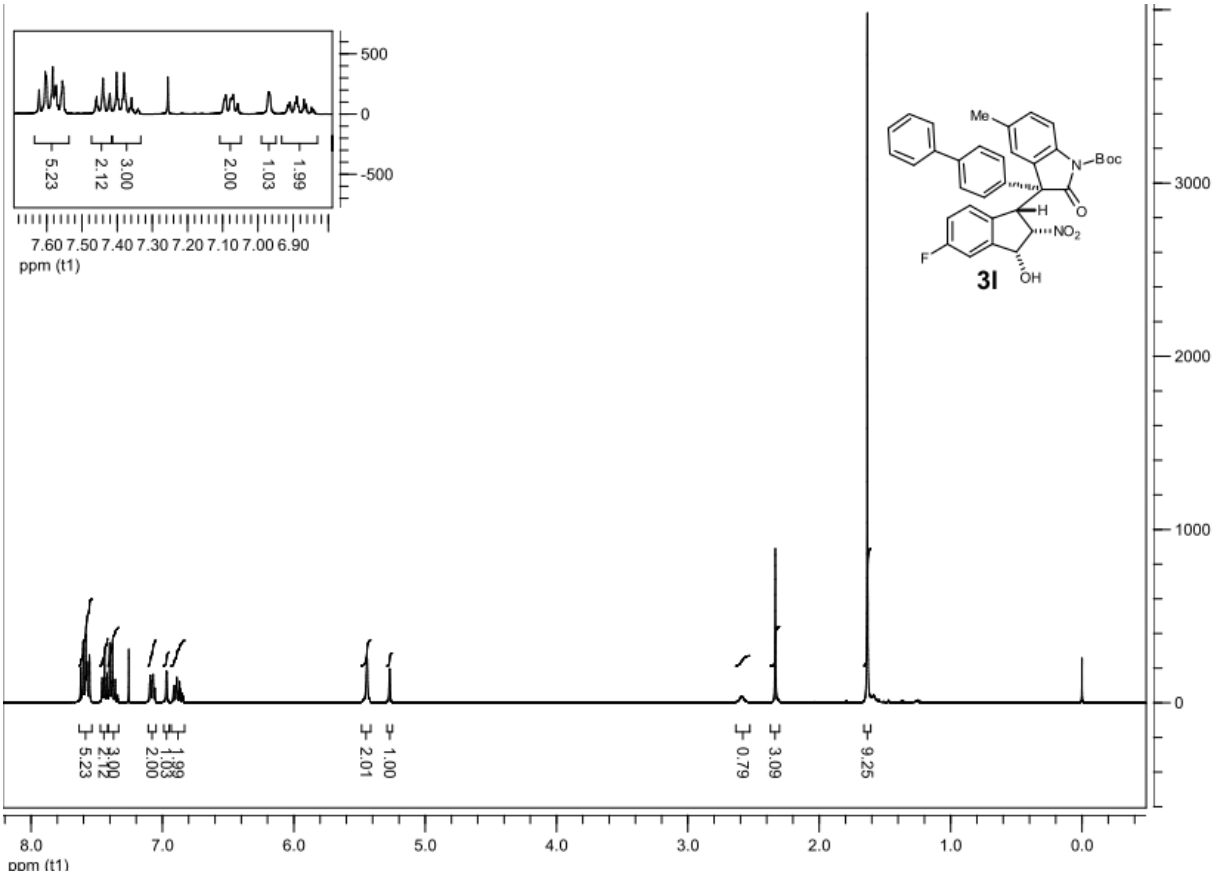
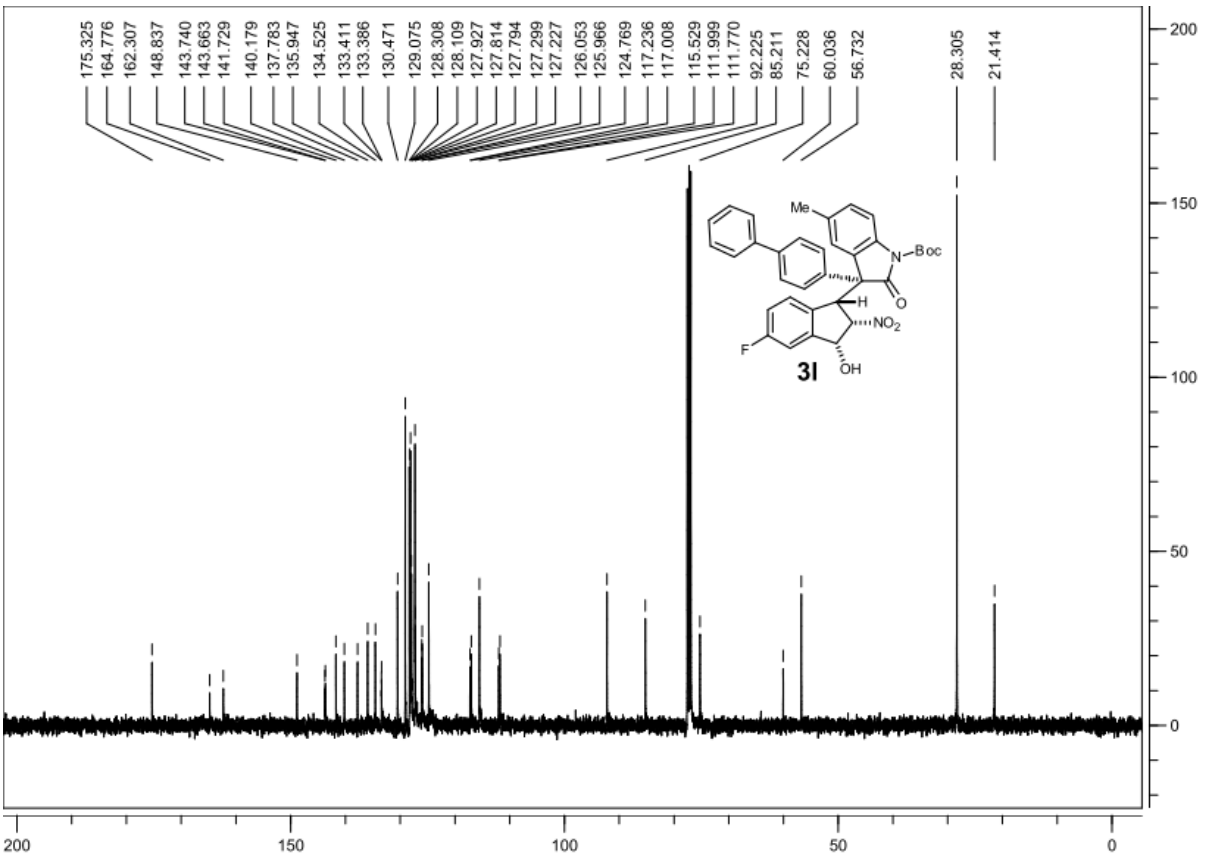
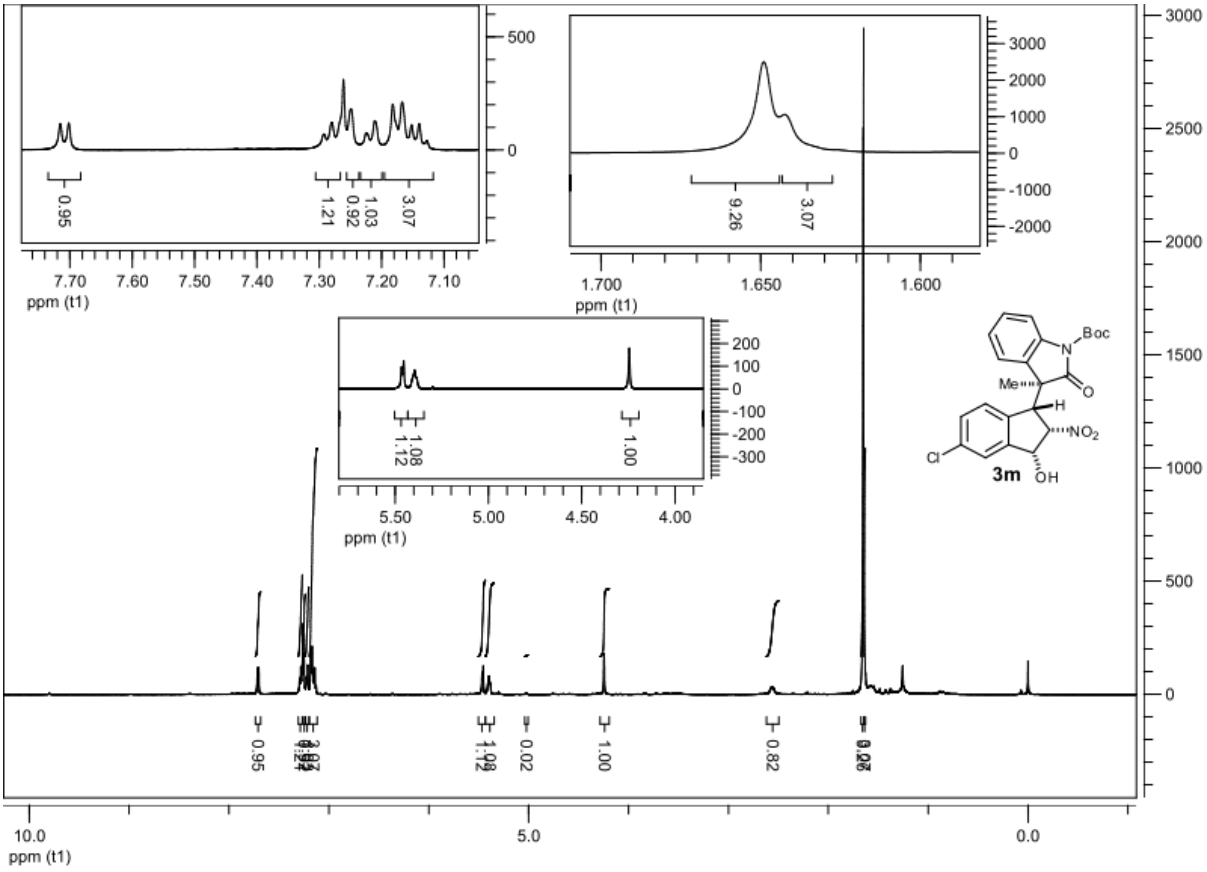
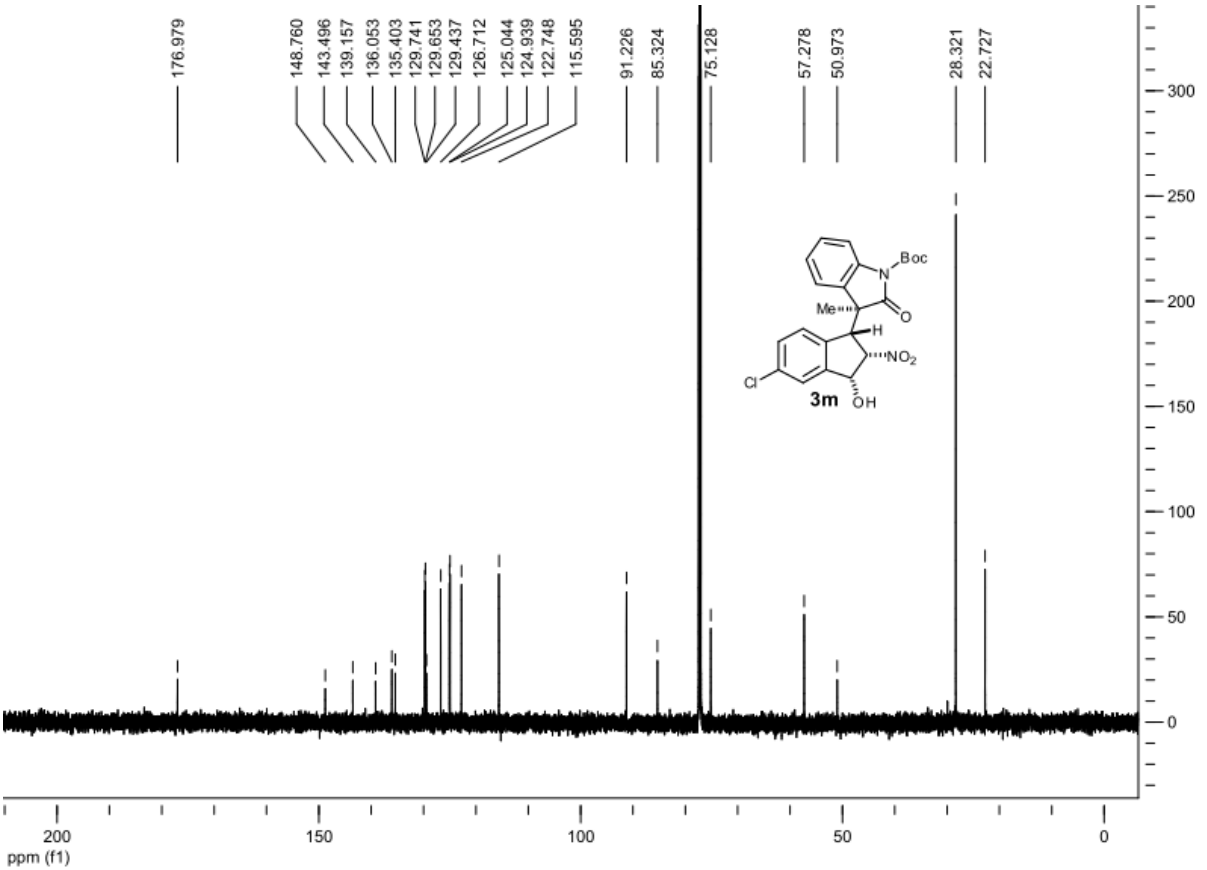
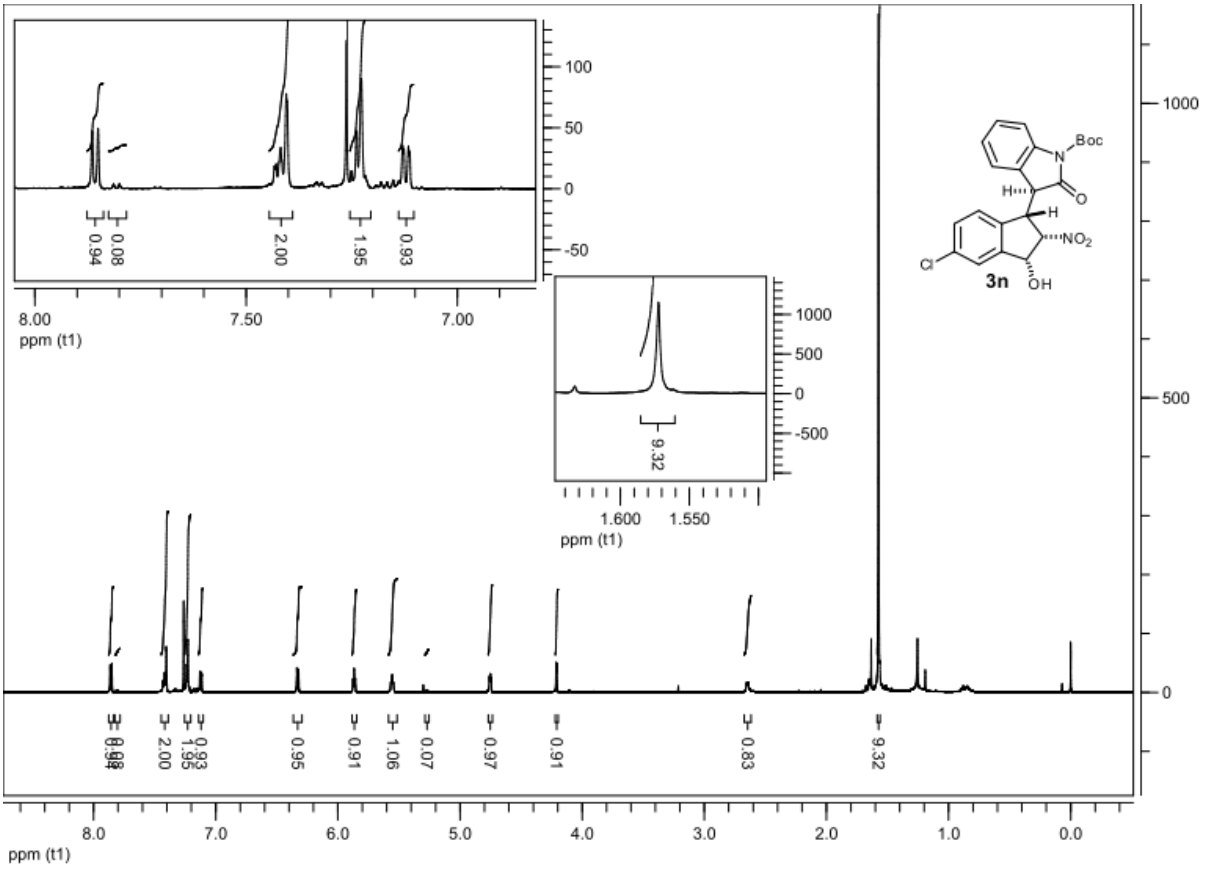
136.224
134.335
130.281
129.629
129.056
128.356
128.043
127.864
127.488
127.311
125.408
124.791
116.646
115.484
108.896
92.398
84.980
75.624
60.149
56.833
55.564
28.319
21.434
Me
N
Boc
O
H
NO2
MeO
OH
3k
200
150
100
50
0

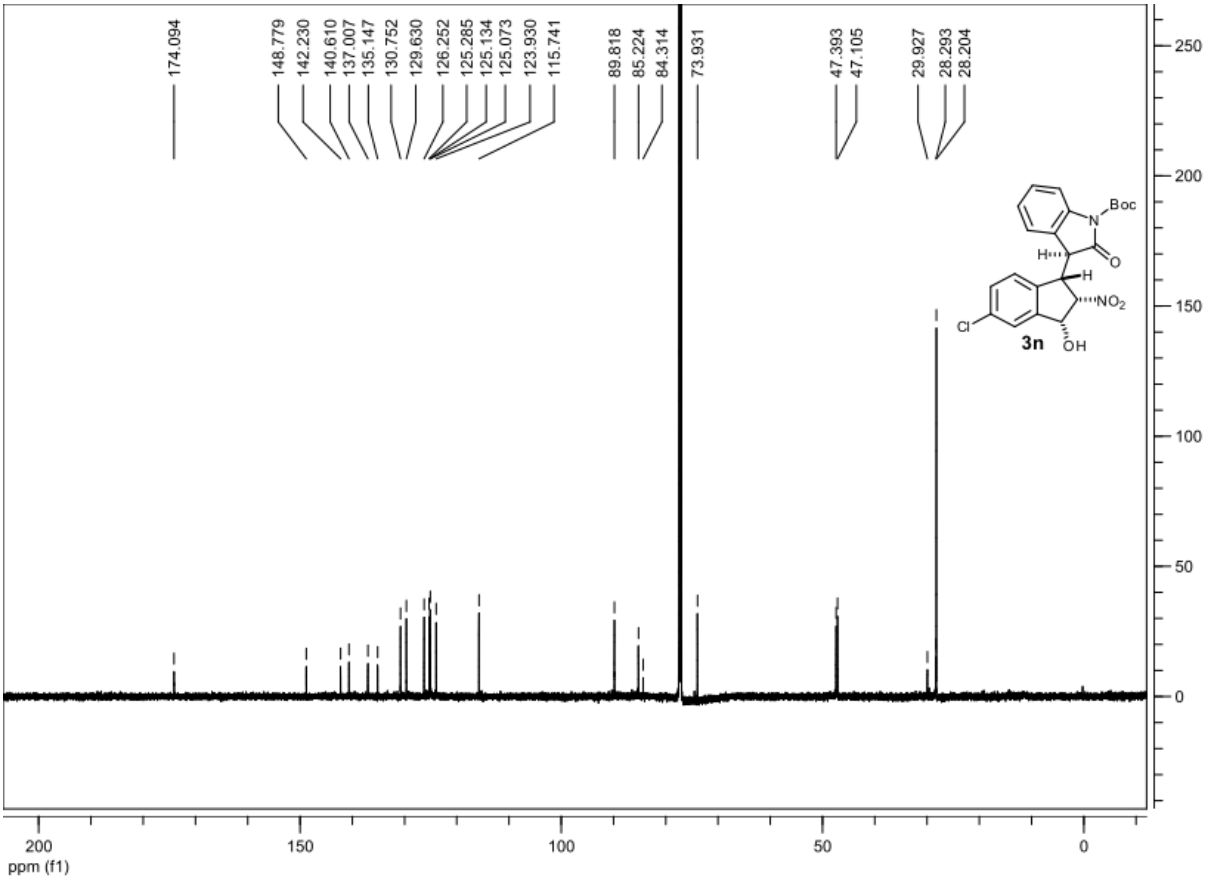

5.23
2.12
3.00
2.00
1.03
1.99
7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90
ppm (t1)
Me
Boc
N
O
H
NO2
F
OH
3l
5.23
3.09
2.00
1.99
2.01
1.00
0.79
3.09
9.25
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

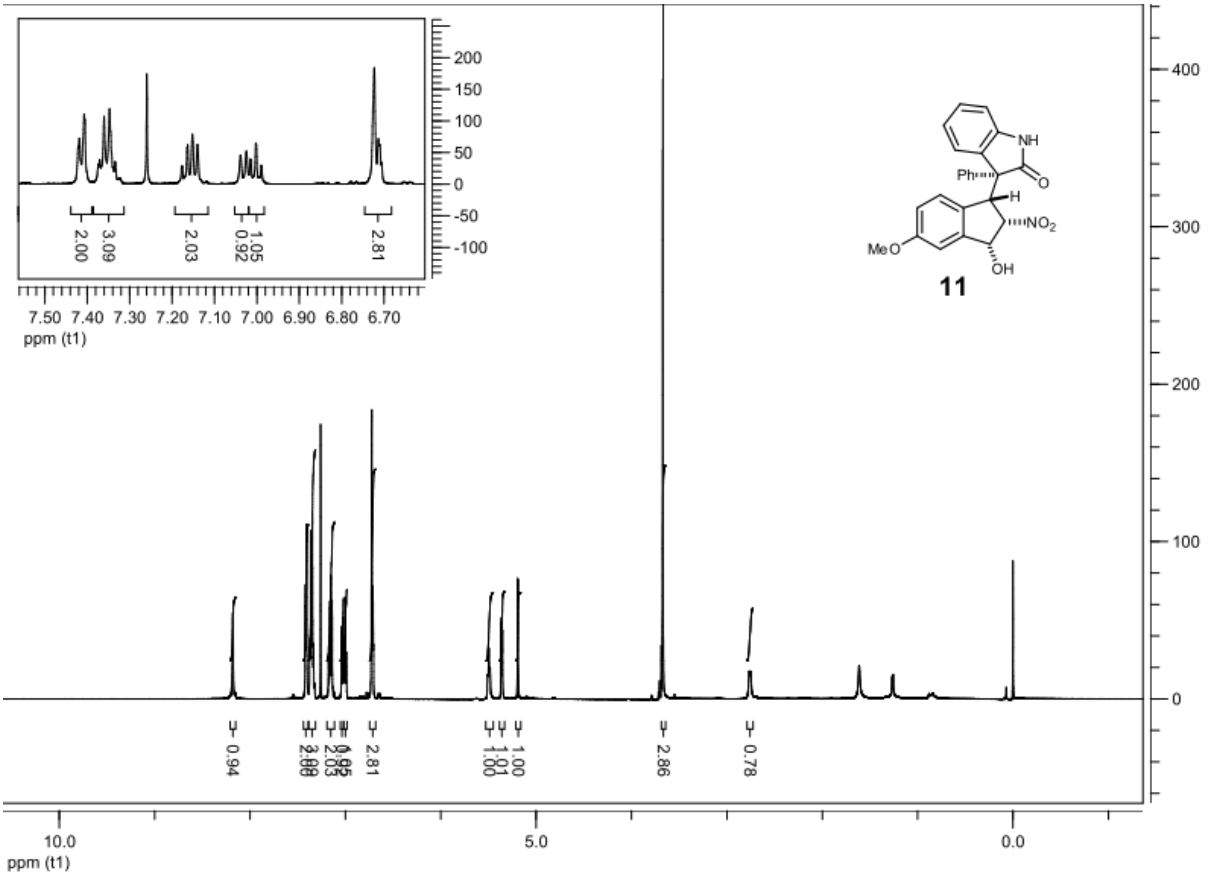

175.325
164.776
162.307
148.837
143.740
143.663
141.729
140.179
137.783
135.947
134.525
133.411
133.386
130.471
129.075
128.308
128.109
127.927
127.814
127.794
127.299
127.227
126.053
125.966
124.769
117.236
117.008
115.529
111.999
111.770
92.225
85.211
75.228
60.036
56.732
28.305
21.414
Me
Boc
N
O
H
NO2
F
OH
3l
200
150
100
50
0

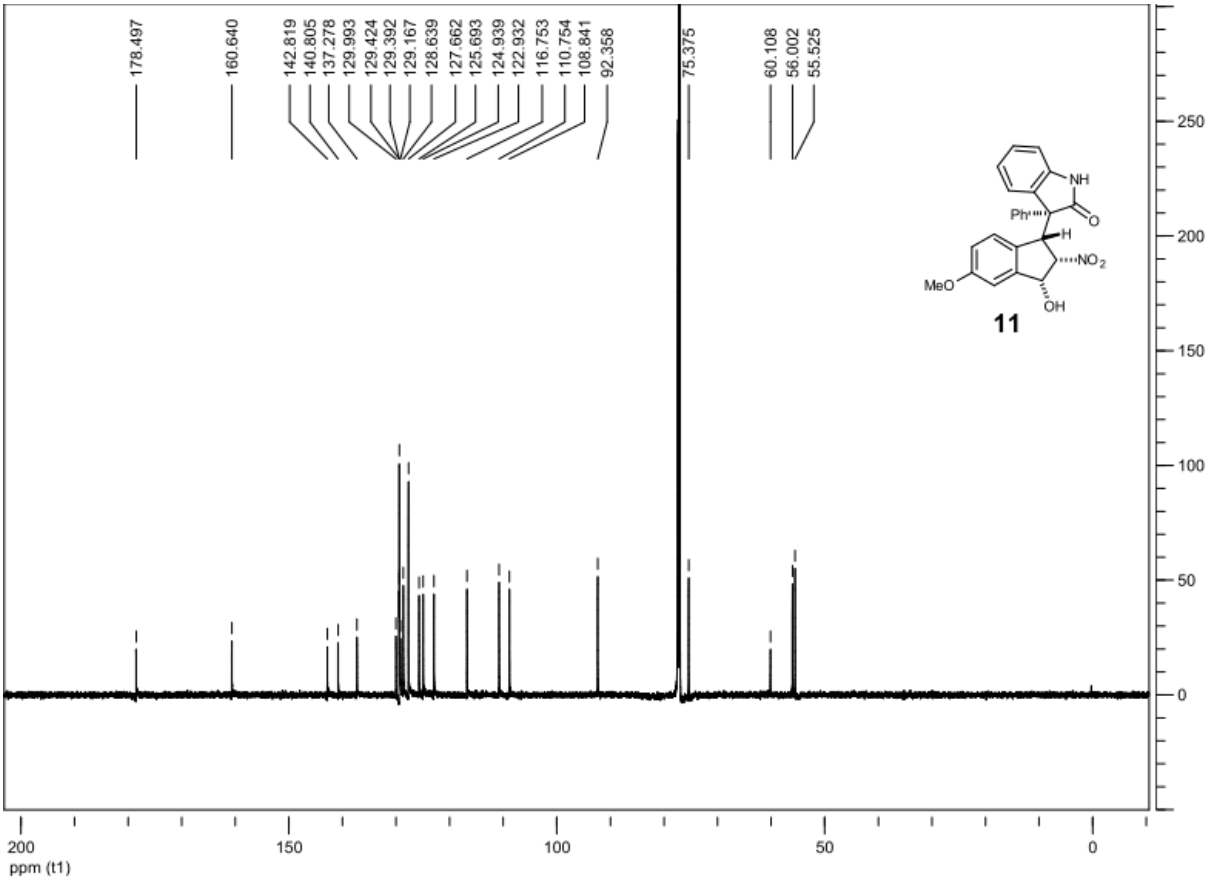

0.95
1.21
0.92
1.03
3.07
9.26
3.07
1.08
1.12
1.00
Boc
Me
H
NO2
Cl
OH
3m
ppm (t1)


176.979
148.760
143.496
139.157
136.053
135.403
129.741
129.653
129.437
126.712
125.044
124.939
122.748
115.595
91.226
85.324
75.128
57.278
50.973
28.321
22.727
Boc
Me
H
NO2
Cl
OH
3m
ppm (f1)


Boc
N
H
O
H
NO2
Cl
OH
3n
ppm (t1)
ppm (t1)


174.094
148.779
142.230
140.610
137.007
135.147
130.752
129.630
126.252
125.285
125.134
125.073
123.930
115.741
89.818
85.224
84.314
73.931
47.393
47.105
29.927
28.293
28.204
Boc
N
H
O
H
NO2
Cl
OH
3n
ppm (f1)


2.00
3.09
2.03
1.05
0.92
2.81
7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80 6.70
ppm (t1)
NH
Ph
O
H
NO2
MeO
OH
11
0.94
2.81
1.00
2.86
0.78
10.0
5.0
0.0
ppm (t1)

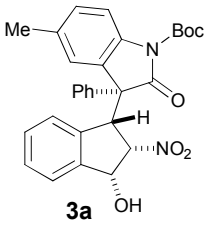

178.497
160.640
142.819
140.805
137.278
129.993
129.424
129.392
129.167
128.639
127.662
125.693
124.939
122.932
116.753
110.754
108.841
92.358
75.375
60.108
56.002
55.525
NH
Ph
O
H
NO2
MeO
OH
11
200
150
100
50
0
ppm (t1)

Chiral HPLC Data

The enantioinductions for product **3a-n** obtained for catalyst **10** (in our methodology, Table 2 in manuscript) are determined by comparing the HPLC data to the opposite enantiomer obtained when catalyst **9** is used.

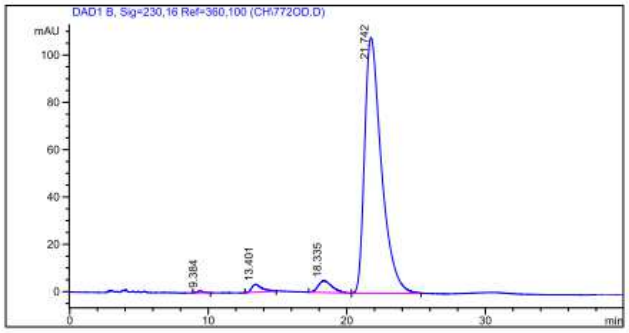
```
Sample Name:          CH 772
Data file:            D:\GONZO\CH\772OD.D
Sample Info:          Laufmittel: n-Heptan/IP  95:5;
                      Die Probe ist in LM/DCM gelöst

Säule:                DAICELOD.M
Säuleninfo:           (250x4,6)mm
Operator:             Analytik Labor AKEN
```

Catalyst **9**



3a

```
Injektion Time:       14:19:13
Injektion Date:       02.04.2013

Instrument Conditions:   At Start          At Stop
Temperature in°C:          30.0°C           30.0°C
Pressure in bar:           26.1             26.6
Flow in ml/min:            1.00             1.00
```

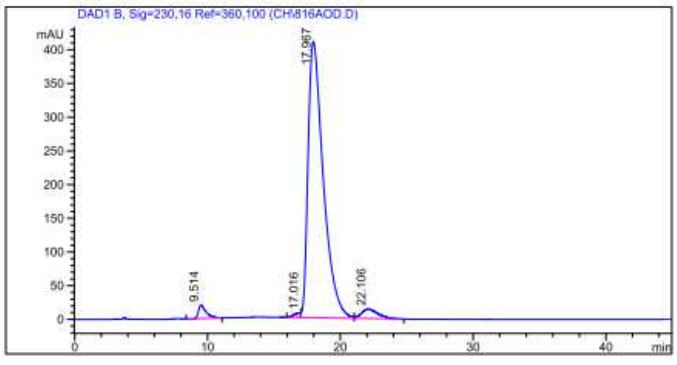


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.38	0.42	0.73	24.74	0.26
2	13.40	0.75	3.32	178.85	1.85
3	18.34	0.89	4.99	349.34	3.61
4	21.74	1.26	108.12	9113.64	94.28
Total				9666.56	100.00

```
Sample Name:          CH 816 A
Data file:            D:\GONZO\CH\816AOD.D
Sample Info:          Laufmittel: n-Heptan/IP  95:5;
                      Die Probe ist in LM/DCM gelöst

Säule:                DAICELOD.M
Säuleninfo:           (250x4,6)mm
Operator:             Analytik Labor AKEN
```

Catalyst **10**

```
Injektion Time:       12:19:44
Injektion Date:       22.05.2013

Instrument Conditions:   At Start          At Stop
Temperature in°C:          30.0°C           30.0°C
Pressure in bar:           36.4             37.6
Flow in ml/min:            1.00             1.00
```

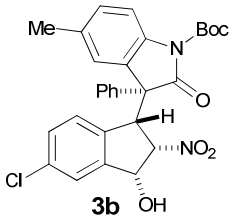


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	9.51	0.58	19.90	801.44	2.30
2	17.02	0.56	6.65	222.93	0.64
3	17.97	1.32	409.77	32562.69	93.56
4	22.11	1.26	13.87	1217.51	3.50
Total				34804.57	100.00

Sample name: **CH 831**
Data file: C:\SNOOPY\CH\CH 831 IC.D
Description: Laufmittel: n-Heptan/EtOH 9:1; Die Probe ist in EtOH/LM gelöst.

Injection date: 5/27/2013 2:57:42 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

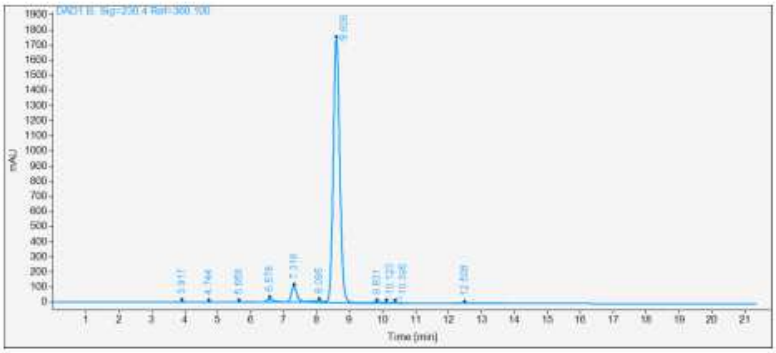
Catalyst **9**



3b

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 18 bar Start flow: 0.500 ml/min Column oven: 30 °C



Name CH 831

RT [min]	Type	Area%	Area	Height	Width [min]
3.92	VV	0.13	32.90	3.38	0.14
4.74	BB	0.01	3.15	0.49	0.10
5.66	BB	0.09	24.31	2.15	0.16
6.58	BB	1.26	331.24	21.09	0.23
7.32	BV	4.89	1280.08	105.78	0.19
8.09	VV	1.21	316.45	10.06	0.42
8.61	VB	91.25	23894.36	1747.96	0.21
9.83	BV	0.46	120.66	7.67	0.24
10.12	VV	0.25	64.60	4.99	0.19
10.39	VB	0.36	93.92	5.99	0.24
12.51	BB	0.10	25.31	1.09	0.34
	Sum	100.00	26186.99		

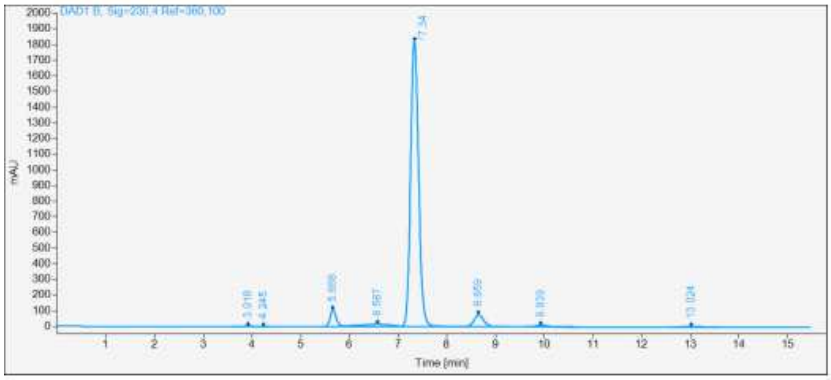
Sample name: **CH 822**
Data file: C:\SNOOPY\CH\CH 822 IC.D
Description: Laufmittel: n-Heptan/EtOH 9:1; Die Probe ist in EtOH/LM gelöst.

Injection date: 5/24/2013 12:52:17 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Catalyst **10**

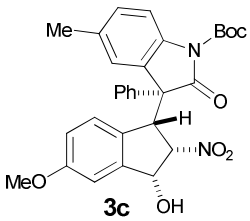
Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 19 bar Start flow: 0.500 ml/min Column oven: 30 °C



Name CH 822

RT [min]	Type	Area%	Area	Height	Width [min]
3.92	BV	0.15	34.79	4.03	0.13
4.24	VB	0.02	4.12	0.60	0.10
5.67	BV	3.96	938.00	109.90	0.13
6.59	VV	2.89	684.60	16.85	0.51
7.34	VB	87.44	20722.68	1825.22	0.17
8.66	BB	4.41	1044.66	76.19	0.21
9.94	BB	0.83	195.61	11.01	0.27
13.02	BB	0.32	75.75	3.41	0.34
	Sum	100.00	23700.22		



3c

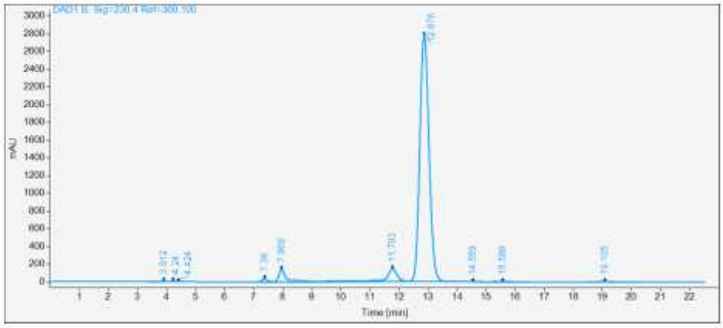
Sample name: **CH 832**
Data file: C:\SNOOPY\CH\CH 832 IC.D
Description: Laufmittel: n-Heptan/EtOH 9:1; Die Probe ist in EtOH/LM gelöst.

Injection date: 5/27/2013 3:21:59 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Catalyst **9**

Pressure at start: 18 bar Start flow: 0.500 ml/min Column oven: 29.99 °C



Name CH 832

RT [min]	Type	Area%	Area	Height	Width [min]
3.91	BV	0.15	106.45	9.06	0.16
4.24	VV	0.08	53.46	6.79	0.12
4.42	VB	0.01	8.11	1.09	0.11
7.38	BV	0.59	412.30	35.38	0.18
7.97	VV	3.64	2529.38	143.88	0.25
11.79	VV	6.76	4703.22	147.13	0.45
12.88	VB	88.22	61363.82	2784.41	0.34
14.56	BB	0.16	108.40	4.92	0.35
15.59	BB	0.16	114.53	3.04	0.61
19.11	BB	0.22	156.11	3.90	0.61
	Sum	100.00	69555.78		

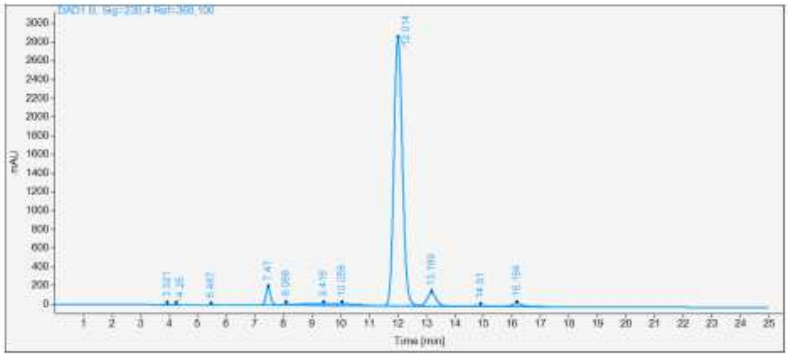
Sample name: **CH 824**
Data file: C:\SNOOPY\CH\824IC.D
Description: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist im LM/DCM gelöst.

Injection date: 5/24/2013 11:26:04 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Catalyst **10**

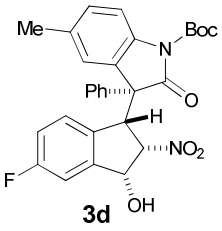
Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 18 bar Start flow: 0.500 ml/min Column oven: 29.97 °C



Name CH 824

RT [min]	Type	Area%	Area	Height	Width [min]
3.92	BV	0.08	52.58	5.53	0.16
4.25	VV	0.06	40.47	6.58	0.10
5.47	BV	0.01	7.78	0.96	0.13
7.47	BB	3.16	2165.96	185.68	0.18
8.09	BV	0.31	213.93	13.55	0.23
9.42	VV	2.09	1432.10	18.22	1.00
10.06	VB	1.46	999.70	19.27	0.67
12.01	BV	86.65	59400.14	2856.15	0.32
13.19	VB	4.65	3188.32	140.64	0.35
14.91	BB	0.31	209.80	8.64	0.38
16.18	BB	1.23	841.35	31.19	0.42
	Sum	100.00	68552.14		



3d

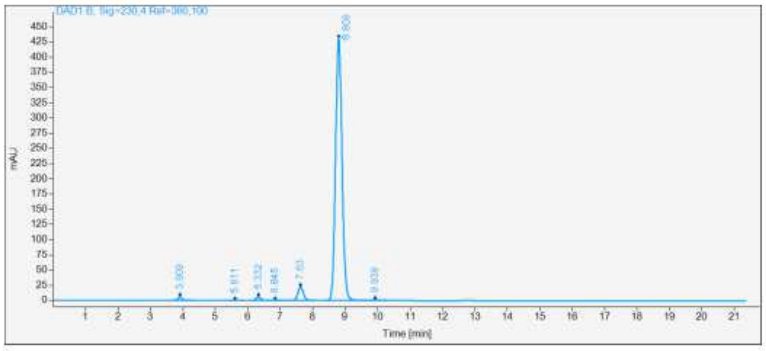
Sample name: **CH 833**
Data file: C:\SNOOPY\CH\CH 833 IC.D
Description: Laufmittel: n-Heptan/EtOH 9:1; Die Probe ist in EtOH/LM gelöst.

Injection date: 5/29/2013 8:21:37 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Catalyst **9**

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 18 bar Start flow: 0.500 ml/min Column oven: 30 °C



Name CH 833

RT [min]	Type	Area%	Area	Height	Width [min]
3.91	BB	0.84	53.67	6.04	0.13
5.61	BB	0.06	3.69	0.43	0.13
6.33	BV	0.86	54.44	5.88	0.14
6.85	VB	0.06	3.70	0.38	0.15
7.63	BB	4.07	259.21	22.23	0.18
8.81	BV	93.76	5965.13	431.32	0.22
9.94	VB	0.35	22.43	1.22	0.29
	Sum	100.00	6362.27		

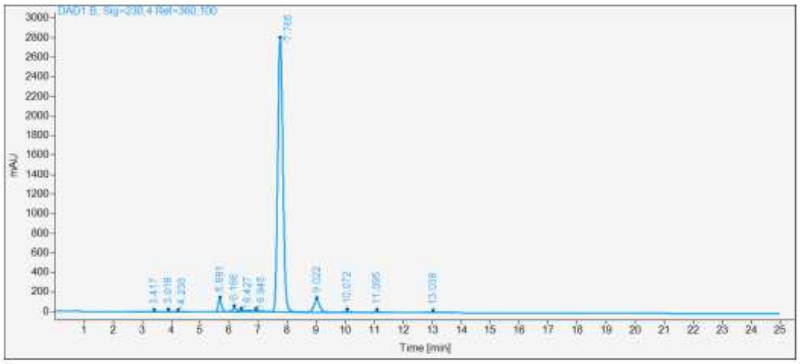
Sample name: **CH 825**
Data file: C:\SNOOPY\CH\825IC.D
Description: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist im LM/DCM gelöst.

Injection date: 5/24/2013 11:52:10 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, S

Catalyst **10**

Pressure at start: 19 bar Start flow: 0.500 ml/min Column oven: 30.02 °C



Name CH 825

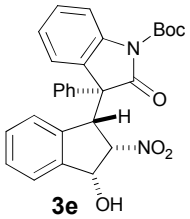
RT [min]	Type	Area%	Area	Height	Width [min]
3.42	BV	0.25	95.85	2.22	0.58
3.92	VV	0.19	74.80	6.58	0.16
4.24	VB	0.03	11.81	1.20	0.13
5.68	BB	2.66	1031.95	126.12	0.13
6.19	BV	1.04	404.34	36.87	0.16
6.43	VV	0.78	300.82	16.07	0.25
6.94	VB	1.05	406.19	16.66	0.33
7.76	BV	88.60	34360.75	2791.15	0.19
9.02	VB	4.63	1794.67	124.48	0.22
10.07	BB	0.41	157.76	9.89	0.25
11.09	BB	0.28	109.86	6.33	0.27
13.04	BBA	0.08	31.98	1.35	0.36
	Sum	100.00	38780.79		

Sample Name: CH 837
Data file: D:\BERT\CH\837W.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst

Agilent Technologies

Säule: WHELK.M
Säuleninfo: (250x4,6)mm

Catalyst **9**

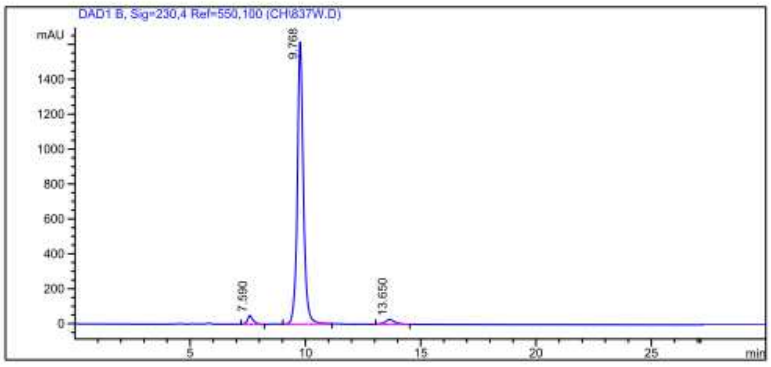


3e

Operator: Analytik Labor AKEN

Injektion Time: 08:47:54
Injektion Date: 04.06.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	32.2	32.1
Flow in ml/min:	0.5	0.5



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.59	0.24	49.94	820.58	2.65
2	9.77	0.27	1615.88	29341.00	94.79
3	13.65	0.40	27.84	793.64	2.56
Total				30955.22	100.00

Sample Name: CH 840
Data file: D:\BERT\CH\840W.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst

Agilent Technologies

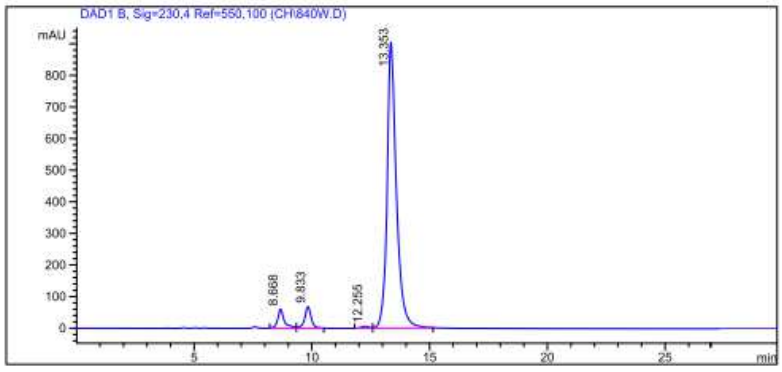
Säule: WHELK.M
Säuleninfo: (250x4,6)mm

Catalyst **10**

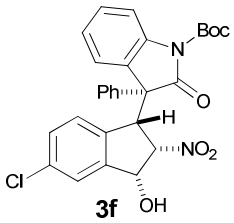
Operator: Analytik Labor

Injektion Time: 09:23:36
Injektion Date: 04.06.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	32.0	32.0
Flow in ml/min:	0.5	0.5



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.67	0.28	59.91	1171.12	4.27
2	9.83	0.28	68.19	1300.17	4.74
3	12.26	0.32	6.14	136.39	0.50
4	13.35	0.40	905.08	24834.27	90.50
Total				27441.95	100.00



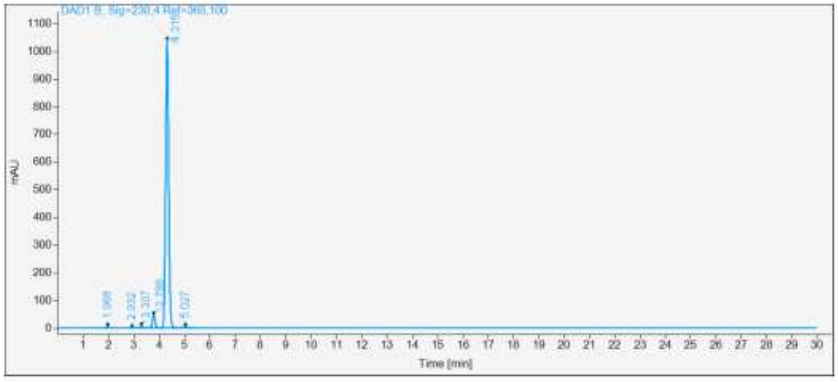
3f

Sample name: **CH 834 S Kat**
Data file: C:\SNOOPY\CH\CH 834SIC.D
Description: Laufmittel: n-Heptan/EtOH 9:1; Die Probe ist im LM/DCM gelöst.
Injection date: 5/31/2013 4:36:26 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Catalyst **9**

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 35 bar Start flow: 1.000 ml/min Column oven: 29.98 °C



Name CH 834 S Kat

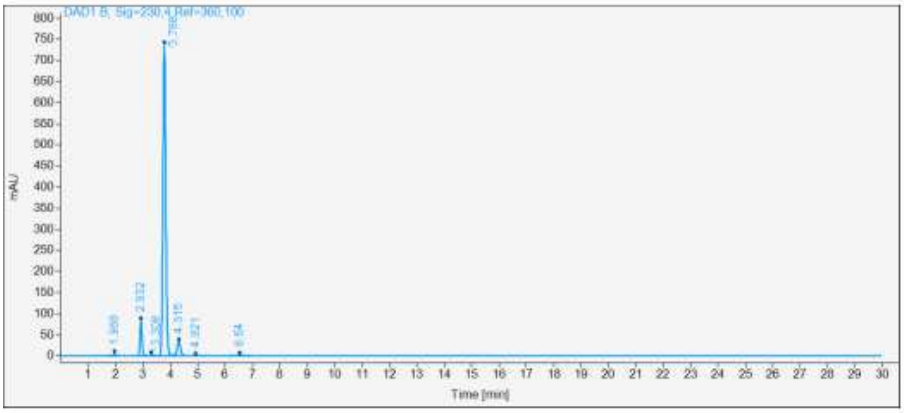
RT [min]	Type	Area%	Area	Height	Width [min]
1.97	BV	0.30	27.02	5.58	0.07
2.93	BB	0.04	3.57	0.55	0.10
3.31	BB	0.43	39.45	6.52	0.09
3.79	BV	3.62	331.16	45.22	0.11
4.32	VV	95.14	8708.20	1039.89	0.13
5.03	VB	0.48	43.80	4.08	0.16
	Sum	100.00	9153.19		

Sample name: **CH 836 R Kat**
Data file: C:\SNOOPY\CH\CH836RIC.D
Description: Laufmittel: n-Heptan/EtOH 9:1; Die Probe ist im LM/DCM gelöst.
Injection date: 5/31/2013 4:05:18 PM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Catalyst **10**

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 35 bar Start flow: 1.000 ml/min Column oven: 29.98 °C



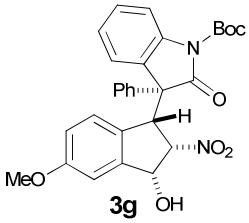
Name CH 836 R Kat

RT [min]	Type	Area%	Area	Height	Width [min]
1.97	BV	0.38	23.16	4.75	0.07
2.93	BV	7.21	437.35	82.65	0.08
3.31	VB	0.37	22.19	3.64	0.10
3.79	BV	87.14	5282.90	738.88	0.11
4.32	VV	4.50	272.89	32.43	0.13
4.92	BB	0.09	5.74	0.57	0.16
6.54	BB	0.30	18.10	1.27	0.22
	Sum	100.00	6062.33		

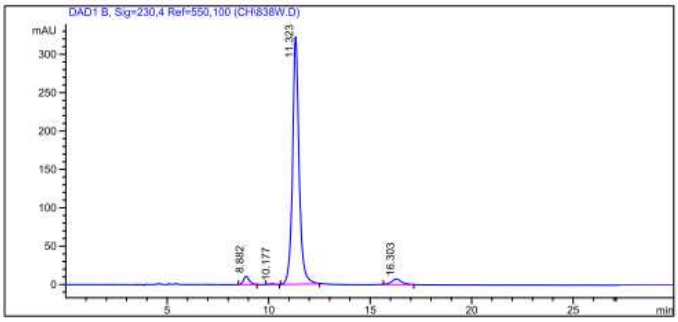
```
Sample Name:      CH 838
Data file:        D:\BERT\CH\838W.D
Sample Info:      Laufmittel: n-Heptan/EtOH 7:3;
                  Die Probe ist in DCM/LM gelöst

Säule:            WHELK.M
Säuleninfo:       (250x4,6)mm

Operator:         Analytik Labor AKEN

Injektion Time:       14:28:48
Injektion Date:       03.06.2013

Instrument Conditions:    At Start              At Stop

Temperature in°C:         30.0                  30.0
Pressure in bar:          31.6                  31.7
Flow in ml/min:           0.5                   0.5
```

Agilent Technologies

Catalyst **9**



3g

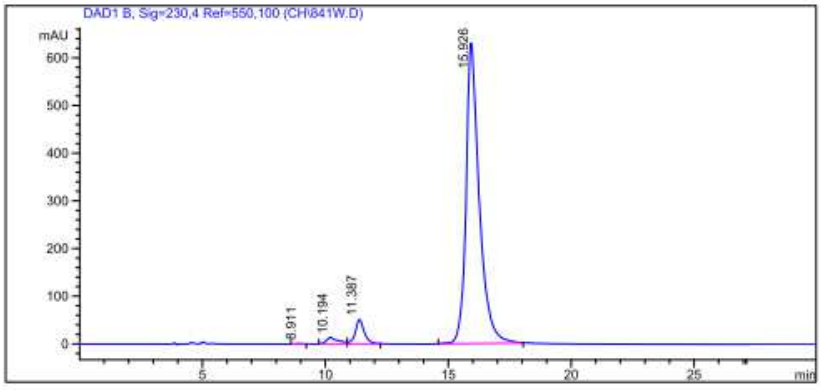


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.88	0.27	11.09	217.79	2.82
2	10.18	0.24	1.07	18.05	0.23
3	11.32	0.33	322.51	7235.97	93.70
4	16.30	0.43	7.22	251.08	3.25
Total				7722.89	100.00

```
Sample Name:      CH 841
Data file:        D:\BERT\CH\841W.D
Sample Info:      Laufmittel: n-Heptan/EtOH 7:3;
                  Die Probe ist in DCM/LM gelöst

Säule:            WHELK.M
Säuleninfo:       (250x4,6)mm

Operator:         Analytik Labor AKEN

Injektion Time:       15:07:15
Injektion Date:       03.06.2013

Instrument Conditions:    At Start              At Stop

Temperature in°C:         30.0                  30.0
Pressure in bar:          31.7                  31.6
Flow in ml/min:           0.5                   0.5
```

Agilent Technologies

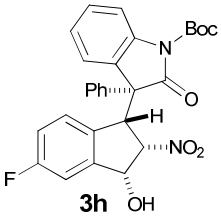
Catalyst **10**



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.91	0.24	1.08	20.33	0.08
2	10.19	0.44	13.56	455.02	1.80
3	11.39	0.36	51.38	1299.97	5.14
4	15.93	0.53	630.23	23531.37	92.98
Total				25306.68	100.00

Sample name: **CH 839**
Data file: C:\SNOOPY\CH\839IC.D
Description: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist im LM/DCM gelöst.
Injection date: 6/3/2013 9:43:48 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

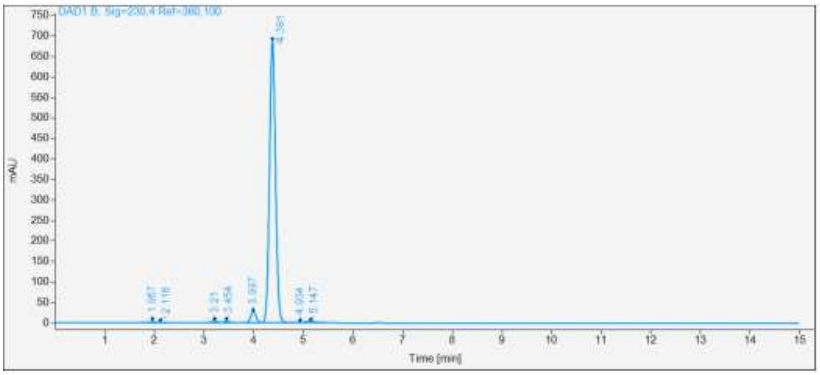
Catalyst **9**



3h

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 36 bar Start flow: 1.000 ml/min Column oven: 29.98 °C



Name CH 839

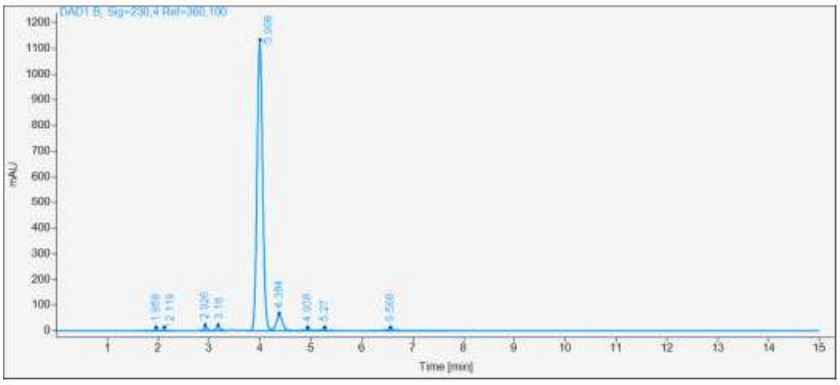
RT [min]	Type	Area%	Area	Height	Width [min]
1.96	BV	0.39	23.88	5.11	0.07
2.12	VV	0.19	11.65	2.51	0.07
3.21	BV	0.57	35.00	5.62	0.10
3.45	VV	0.52	31.80	5.05	0.10
4.00	BV	3.33	205.03	27.34	0.12
4.38	VV	94.00	5795.63	688.74	0.13
4.93	VV	0.28	17.15	1.87	0.14
5.15	VB	0.73	45.23	3.93	0.17
	Sum	100.00	6165.38		

Sample name: **CH 842**
Data file: C:\SNOOPY\CH\842IC.D
Description: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist im LM/DCM gelöst.
Injection date: 6/3/2013 9:59:54 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Column: Chiralpak IC, (150 x 4,6) mm,

Catalyst **10**

Pressure at start: 36 bar Start flow: 1.000 ml/min Column oven: 29.98 °C

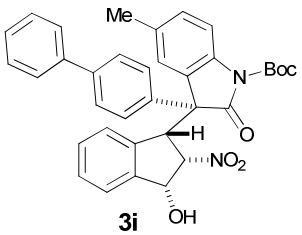


Name CH 842

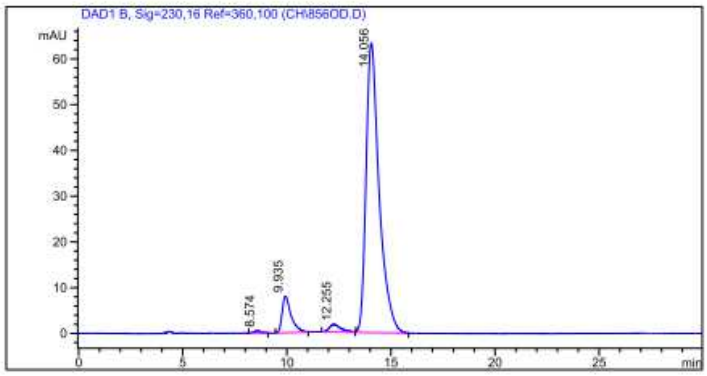
RT [min]	Type	Area%	Area	Height	Width [min]
1.96	BV	0.25	23.27	4.98	0.07
2.12	VV	0.15	14.14	3.40	0.06
2.93	BB	0.70	65.07	12.48	0.08
3.18	BV	0.85	79.25	13.53	0.09
4.00	BV	91.11	8527.25	1125.81	0.12
4.38	VB	5.34	499.36	58.44	0.13
4.94	BV	0.45	42.14	4.47	0.15
5.27	VB	0.48	44.59	4.35	0.16
6.57	BB	0.68	63.77	4.53	0.22
	Sum	100.00	9358.84		

```
Sample Name:          CH 856
Data file:            D:\GONZO\CH\856OD.D
Sample Info:          Laufmittel: n-Heptan/EtOH  9:1;
                      Die Probe ist in LM gelöst

Säule:                DAICELOD.M
Säuleninfo:           (250x4,6)mm
Operator:             Analytik Labor AKEN

Injektion Time:       15:36:38
Injektion Date:       19.06.2013

Instrument Conditions:   At Start          At Stop
Temperature in°C:          30.0°C           30.0°C
Pressure in bar:           17.6             17.9
Flow in ml/min:            0.70             0.70
```

Catalyst **9**



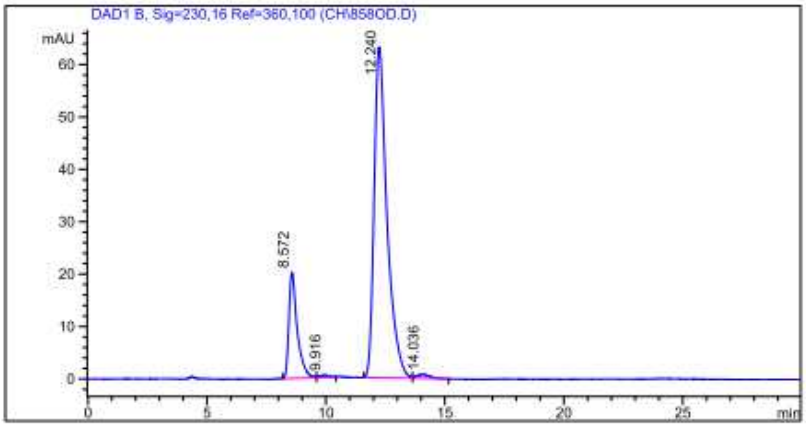
3i



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.57	0.33	0.51	11.59	0.38
2	9.94	0.44	8.02	239.24	7.77
3	12.26	0.59	1.68	67.88	2.20
4	14.06	0.65	63.34	2761.84	89.65
Total				3080.55	100.00

```
Sample Name:          CH 858
Data file:            D:\GONZO\CH\858OD.D
Sample Info:          Laufmittel: n-Heptan/EtOH  9:1;
                      Die Probe ist in LM gelöst

Säule:                DAICELOD.M
Säuleninfo:           (250x4,6)mm
Operator:             Analytik Labor AKEN

Injektion Time:       16:07:51
Injektion Date:       19.06.2013

Instrument Conditions:   At Start          At Stop
Temperature in°C:          30.0°C           30.0°C
Pressure in bar:           17.4             18.0
Flow in ml/min:            0.70             0.70
```

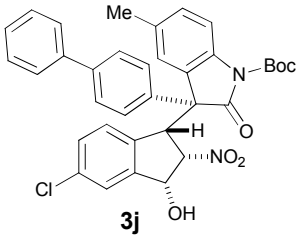
Catalyst **10**



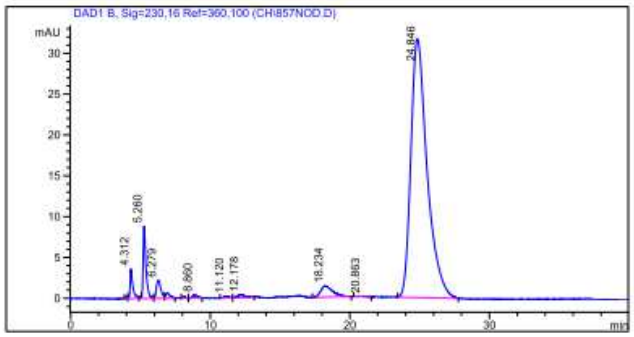
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.57	0.36	20.29	493.95	16.97
2	9.92	0.38	0.49	13.59	0.47
3	12.24	0.56	63.11	2374.23	81.55
4	14.04	0.49	0.76	29.57	1.02
Total				2911.33	100.00

```
Sample Name:          CH 857 neu
Data file:            D:\GONZO\CH\857NOD.D
Sample Info:          Laufmittel: n-Heptan/EtOH  95:5;
                      Die Probe ist in LM gelöst

Säule:                DAICELOD.M
Säuleninfo:           (250x4,6)mm
Operator:             Analytik Labor AKEN

 Injektion Time:       11:13:45
 Injektion Date:       24.06.2013

 Instrument Conditions:   At Start          At Stop
 Temperature in°C:          30.0°C           30.0°C
 Pressure in bar:           16.8             17.0
 Flow in ml/min:            0.70             0.70
```

Catalyst **9**



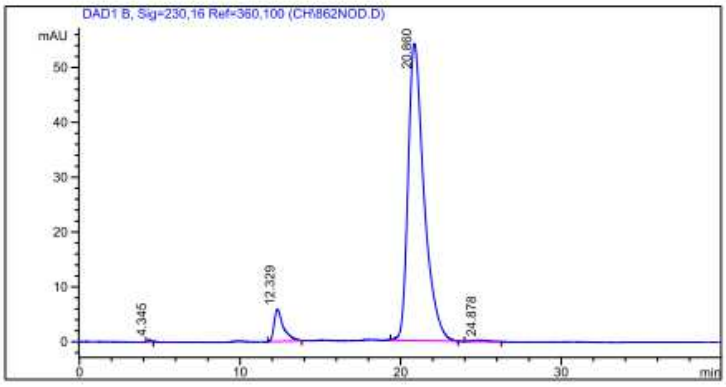
3j



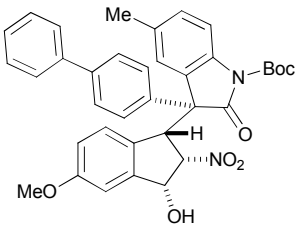
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.00	0.12	0.29	2.34	0.08
2	4.31	0.19	3.64	50.14	1.72
3	5.26	0.20	8.85	124.12	4.25
4	6.28	0.34	2.22	49.47	1.70
5	6.92	0.32	0.70	15.31	0.52
6	8.10	0.21	0.18	2.94	0.10
7	8.86	0.37	0.39	10.14	0.35
8	11.12	0.35	0.23	5.91	0.20
9	12.18	0.54	0.34	14.99	0.51
10	18.23	0.79	1.37	83.75	2.87
11	20.86	0.66	0.06	2.47	0.08
12	24.85	1.20	31.66	2555.75	87.61
Total				2917.34	100.00

```
Sample Name:          CH 862 neu
Data file:            D:\GONZO\CH\862NOD.D
Sample Info:          Laufmittel: n-Heptan/EtOH  95:5;
                      Die Probe ist in LM gelöst

Säule:                DAICELOD.M
Säuleninfo:           (250x4,6)mm
Operator:             Analytik Labor AKEN

 Injektion Time:       11:54:56
 Injektion Date:       24.06.2013

 Instrument Conditions:   At Start          At Stop
 Temperature in°C:          30.0°C           30.0°C
 Pressure in bar:           16.9             17.1
 Flow in ml/min:            0.70             0.70
```

Catalyst **10**



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.34	0.20	0.43	5.35	0.13
2	12.33	0.58	5.90	237.32	5.94
3	20.86	1.03	54.17	3730.79	93.44
4	24.88	1.13	0.28	19.13	0.48
Total				3992.59	100.00



3k

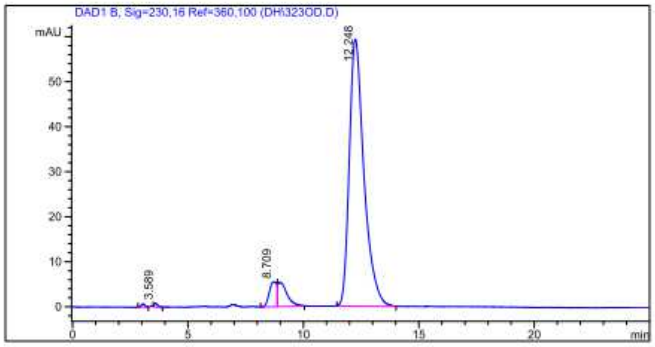
Sample Name: DH 323
Data file: D:\GONZO\DH\323OD.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst.

Säule: DAICELOD.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Catalyst **9**

Injektion Time: 09:57:47
Injektion Date: 20.06.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	27.0	27.5
Flow in ml/min:	1.00	1.00



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.04	0.16	0.76	8.63	0.30
2	3.59	0.14	0.94	8.94	0.31
3	8.71	0.34	5.53	123.72	4.25
4	8.99	0.42	5.34	153.54	5.28
5	12.25	0.66	59.38	2613.89	89.86
Total				2908.72	100.00

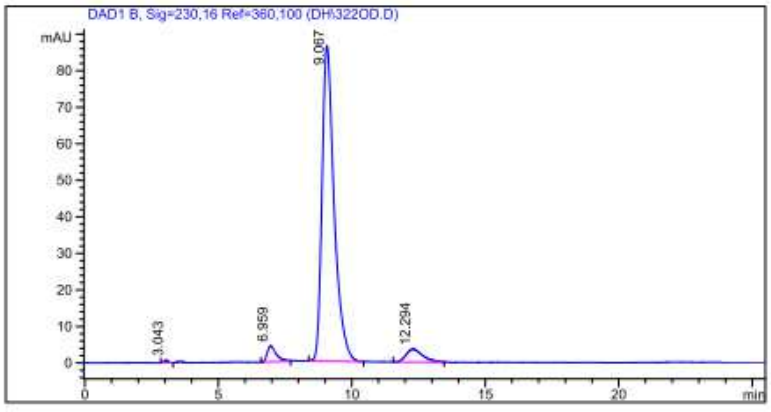
Sample Name: DH 322
Data file: D:\GONZO\DH\322OD.D
Sample Info: Laufmittel: n-Heptan/EtOH 9:1;
Die Probe ist in DCM/LM gelöst.

Säule: DAICELOD.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

Catalyst **10**

Injektion Time: 09:30:03
Injektion Date: 20.06.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	26.9	27.4
Flow in ml/min:	1.00	1.00



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.04	0.14	0.79	7.85	0.26
2	6.96	0.35	4.44	104.92	3.51
3	9.07	0.47	86.36	2721.39	90.99
4	12.29	0.64	3.57	156.63	5.24
Total				2990.79	100.00

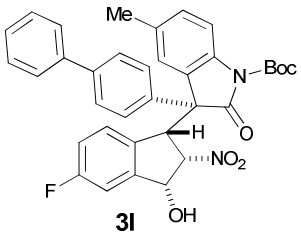
HEWLETT PACKARD

Sample Name: DH 325
Data file: D:\GONZO\DH\325OD.D
Sample Info: Laufmittel: n-Heptan/EtOH 95:5;
Die Probe ist in LM gelöst

Säule: DAICELOD.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

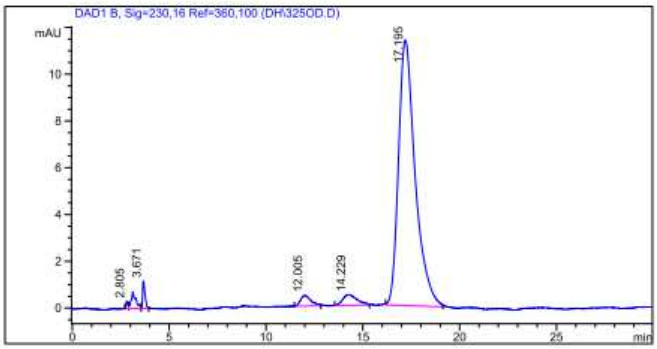
Injektion Time: 11:31:54
Injektion Date: 21.06.2013

Catalyst **9**



3l

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	25.8	26.0
Flow in ml/min:	1.00	1.00



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	2.80	0.10	0.32	2.07	0.28
2	3.12	0.22	0.71	12.27	1.65
3	3.67	0.13	1.18	10.61	1.43
4	12.01	0.47	0.46	17.35	2.34
5	14.23	0.63	0.45	23.54	3.17
6	17.19	0.89	11.36	676.86	91.13
Total				742.70	100.00

HEWLETT PACKARD

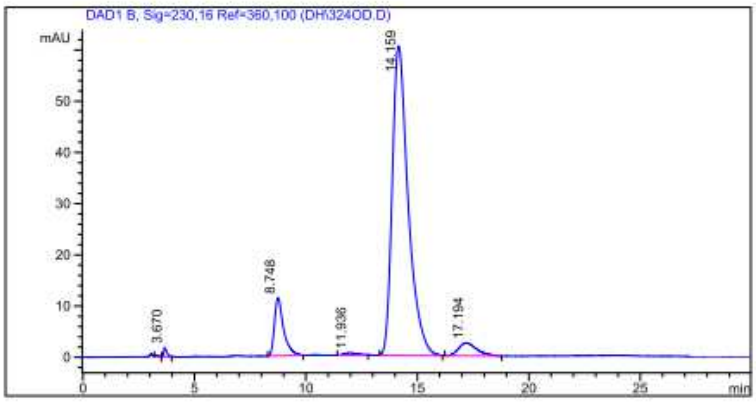
Sample Name: DH 324
Data file: D:\GONZO\DH\324OD.D
Sample Info: Laufmittel: n-Heptan/EtOH 95:5;
Die Probe ist in DCM/LM gelöst.

Säule: DAICELOD.M
Säuleninfo: (250x4,6)mm
Operator: Analytik Labor AKEN

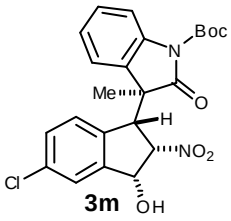
Injektion Time: 10:24:58
Injektion Date: 21.06.2013

Catalyst **10**

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	25.6	26.0
Flow in ml/min:	1.00	1.00



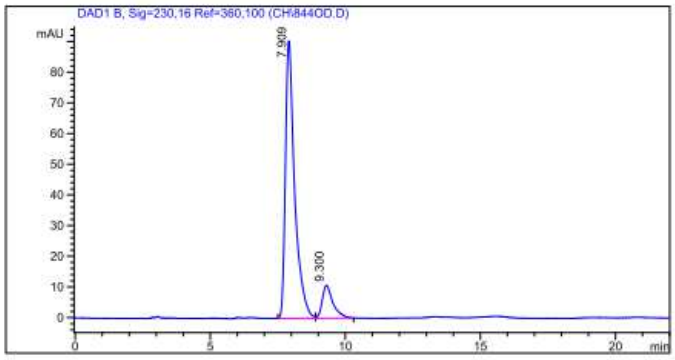
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.27	0.11	0.39	3.01	0.09
2	3.67	0.13	1.84	16.82	0.48
3	8.75	0.42	11.34	320.74	9.13
4	11.94	0.54	0.48	21.35	0.61
5	14.16	0.75	60.49	3005.56	85.57
6	17.19	0.84	2.53	145.05	4.13
Total				3512.53	100.00



3m

Catalyst **9**

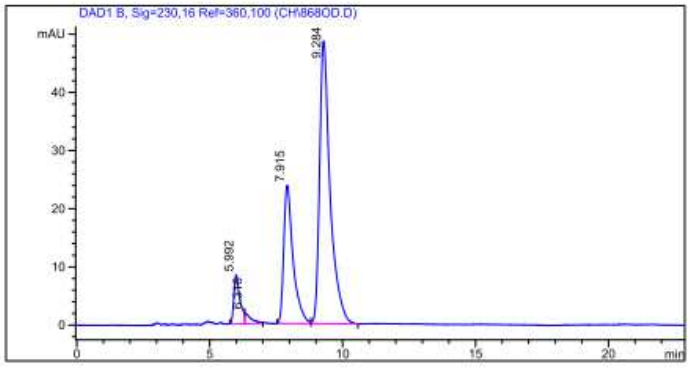
```
Sample Name:          CH 844
Data file:            D:\GONZO\CH\844OD.D
Sample Info:          Laufmittel: n-Heptan/EtOH 9:1:;
                      Die Probe ist in LM/EtOH gelöst.

Säule:                DAICELOD.M
Säuleninfo:           Chiralcel OD (250x4,6)mm
Operator:             Analytik Labor AKEN

 Injektion Time:       09:22:57
 Injektion Date:       28.08.2013

 Instrument Conditions:   At Start          At Stop
 Temperature in°C:          30.0°C           30.0°C
 Pressure in bar:           28.1             28.4
 Flow in ml/min:            1.00             1.00
```



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.91	0.35	90.50	2149.47	87.92
2	9.30	0.41	10.73	295.36	12.08
Total				2444.83	100.00

```
Sample Name:          CH 868
Data file:            D:\GONZO\CH\868OD.D
Sample Info:          Laufmittel: n-Heptan/EtOH 9:1:;
                      Die Probe ist in LM/EtOH gelöst.

Säule:                DAICELOD.M
Säuleninfo:           Chiralcel OD (250x4,6)mm
Operator:             Analytik Labor AKEN

 Injektion Time:       09:46:29
 Injektion Date:       28.08.2013

 Instrument Conditions:   At Start          At Stop
 Temperature in°C:          30.0°C           30.0°C
 Pressure in bar:           27.8             28.3
 Flow in ml/min:            1.00             1.00
```

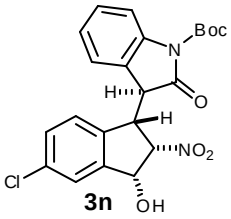
Catalyst **10**



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.99	0.27	8.39	134.22	6.43
2	6.32	0.27	1.91	30.57	1.47
3	6.82	0.00	0.20	0.00	0.00
4	7.92	0.36	23.73	578.92	27.75
5	9.28	0.41	48.60	1342.31	64.35
Total				2086.03	100.00

Sample name: **CH 870**
Data file: C:\SNOOPY\CH\870IC.D
Description: Laufmittel: n-Heptan/IP 8:2;
Die Probe ist im LM/DCM gelöst.
Injection date: 9/3/2013 10:03:57 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

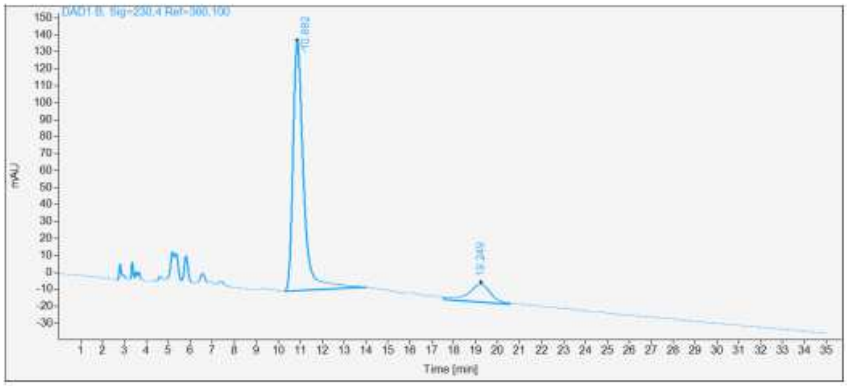
Catalyst **9**



3n

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 26 bar Start flow: 0.700 ml/min Column oven: 29.98 °C



Name CH 870

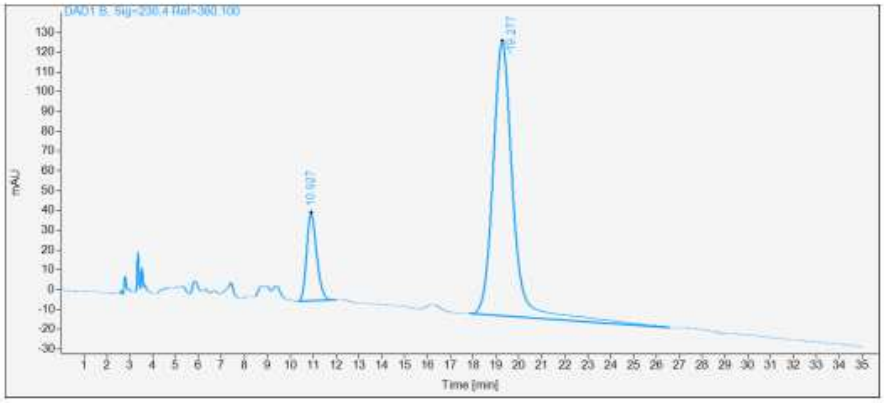
RT [min]	Type	Area%	Area	Height	Width [min]
10.88	MM	86.28	4917.42	146.60	0.56
19.25	MM	13.72	782.03	10.73	1.22
	Sum	100.00	5699.45		

Sample name: **CH 869**
Data file: C:\SNOOPY\CH\869IC.D
Description: Laufmittel: n-Heptan/IP 8:2;
Die Probe ist im LM/DCM gelöst.
Injection date: 9/3/2013 9:27:50 AM
Acq. Analysis method: CHIRALPAKIC1-6LNP.M

Catalyst **10**

Column: Chiralpak IC, (150 x 4,6) mm, 5µ, SN: IC00CD-QF015

Pressure at start: 26 bar Start flow: 0.700 ml/min Column oven: 29.97 °C



Name CH 869

RT [min]	Type	Area%	Area	Height	Width [min]
10.93	BB	13.65	1342.35	43.78	0.47
19.28	BB	86.35	8492.35	138.00	0.92
	Sum	100.00	9834.70		

Sample Name: CH 838
Data file: D:\BERT\CH\838W.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst

Agilent Technologies

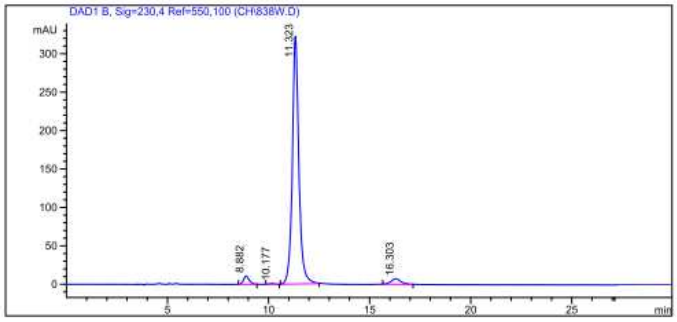
Säule: WHELK.M
Säuleninfo: (250x4,6)mm

Catalyst **9**

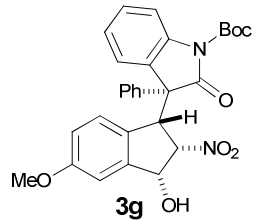
Operator: Analytik Lab

Injektion Time: 14:28:48
Injektion Date: 03.06.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	31.6	31.7
Flow in ml/min:	0.5	0.5



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.88	0.27	11.09	217.79	2.82
2	10.18	0.24	1.07	18.05	0.23
3	11.32	0.33	322.51	7235.97	93.70
4	16.30	0.43	7.22	251.08	3.25
Total				7722.89	100.00



3g

Sample Name: CH 864
Data file: D:\BERT\CH\864NW.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst

Agilent Technologies

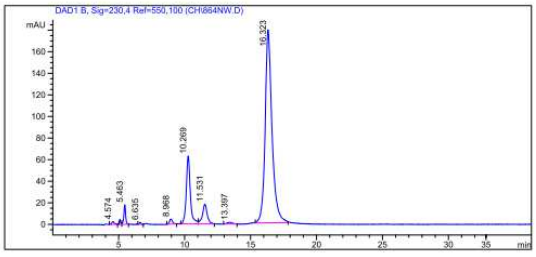
Säule: WHELK.M
Säuleninfo: (250x4,6)mm

Catalyst **10 (Gram Scale)**
after column

Operator: Analytik Labor AKEN

Injektion Time: 13:09:21
Injektion Date: 28.06.2013

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	32.2	32.5
Flow in ml/min:	0.5	0.5



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.57	0.20	2.63	38.73	0.45
2	5.09	0.09	4.63	28.35	0.33
3	5.46	0.14	18.11	168.55	1.95
4	6.63	0.14	1.83	17.45	0.20
5	8.97	0.23	4.66	77.20	0.89
6	10.27	0.31	62.92	1341.09	15.49
7	11.53	0.36	18.30	464.92	5.37
8	13.40	0.33	1.60	43.91	0.51
9	16.32	0.52	178.83	6476.72	74.82
Total				8656.91	100.00

Sample Name: CH 864 recry
Data file: D:\BERT\CH\864REW.D
Sample Info: Laufmittel: n-Heptan/EtOH 7:3;
Die Probe ist in DCM/LM gelöst

Agilent Technologies

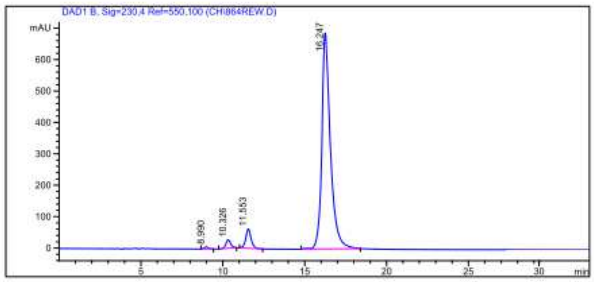
Säule: WHELK.M
Säuleninfo: (s,s)-Whelk O1 (250x4,6)m

Catalyst **10 (Gram Scale)**
after trituration in Et_2O

Operator: Analytik Labor AKEN

Injektion Time: 08:08:13
Injektion Date: 28.06.2013

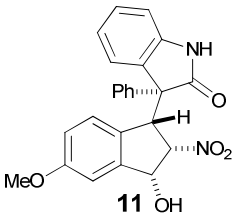
Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0	30.0
Pressure in bar:	33.4	32.6
Flow in ml/min:	0.5	0.5



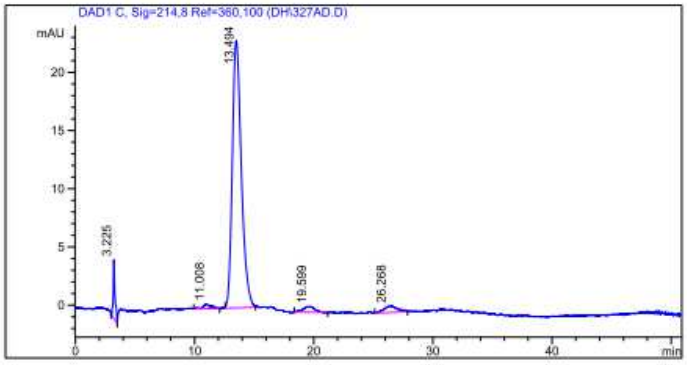
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.99	0.27	6.64	119.19	0.44
2	10.33	0.34	27.63	569.13	2.10
3	11.55	0.38	61.73	1405.91	5.20
4	16.25	0.52	687.24	24967.80	92.26
Total				27062.03	100.00

```
Sample Name:          DH 327
Data file:            D:\GONZO\DH\327AD.D
Sample Info:          Laufmittel: n-Heptan/EtOH  7:3;
                      Die Probe ist in LM gelöst

Säule:                DAICELAD.M
Säuleninfo:           (250x4,6)mm
Operator:             Analytik Labor AKEN

 Injektion Time:       09:27:03
 Injektion Date:       04.07.2013

 Instrument Conditions:   At Start          At Stop
 Temperature in°C:          30.0°C           30.0°C
 Pressure in bar:           30.8             31.1
 Flow in ml/min:            1.00             1.00
```

derived from Catalyst **9**



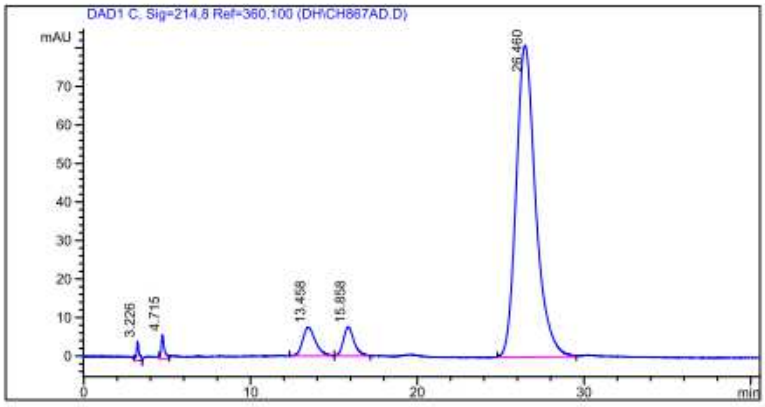
11



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.22	0.15	5.07	52.18	3.85
2	11.01	0.56	0.41	18.23	1.34
3	13.49	0.79	22.99	1208.19	89.05
4	19.60	0.82	0.49	33.86	2.50
5	26.27	0.98	0.54	44.33	3.27
Total				1356.79	100.00

```
Sample Name:          DH CH 867
Data file:            D:\GONZO\DH\CH867AD.D
Sample Info:          Laufmittel: n-Heptan/EtOH  7:3;
                      Die Probe ist in LM gelöst

Säule:                DAICELAD.M
Säuleninfo:           (250x4,6)mm
Operator:             Analytik Labor AKEN

 Injektion Time:       10:19:14
 Injektion Date:       04.07.2013

 Instrument Conditions:   At Start          At Stop
 Temperature in°C:          30.0°C           30.0°C
 Pressure in bar:           30.6             31.3
 Flow in ml/min:            1.00             1.00
```

derived from Catalyst **10**



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.23	0.15	4.95	52.69	0.71
2	4.71	0.19	6.27	83.98	1.13
3	13.46	0.75	7.49	401.97	5.40
4	15.86	0.70	7.51	336.06	4.51
5	26.46	1.24	80.98	6573.43	88.26
Total				7448.13	100.00