Supporting Information

Rhodium(II)–Catalyzed Enantioselective C–H Functionalization of Indoles

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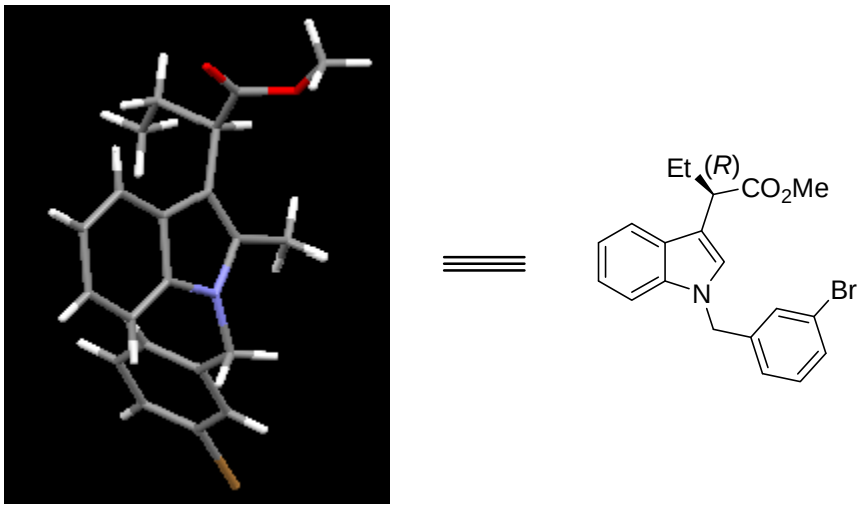
General Considerations

All reactions were carried out in glassware that was flame-dried under vacuum and cooled under nitrogen. Toluene, diethyl ether, hexanes, methylene chloride, and acetonitrile were dried with columns packed with activated neutral alumina and degassed with nitrogen prior to use. THF was distilled from sodium/benzophenone. Chromatography was performed on silica gel (silicycle 40-63D, 60Å). For ^{13}C NMR, multiplicities were distinguished using an ATP pulse sequence: typical methylene and quaternary carbons appear 'up' (u); methine and methyl carbons appear 'down' (dn). NMR yields were determined by addition of 1 equivalent of methyl *tert*-butyl ether as an internal standard to the crude reaction mixture. Reagents were used directly as purchased from commercial sources without further purification. Ethyl 2-diazopropanoate, ethyl 2-diazobutanoate, ethyl 2-diazohexanoate, ethyl 2-diazooctanoate, ethyl 2-diazo-5-methylhexanoate, methyl 2-diazobutanoate, and propyl 2-diazobutanoate were prepared from the corresponding β-ketoesters according to literature protocol.[1] 1-Phenylindole,[2] 2-methyl-1-phenylindole,[3] 1-benzyl-2-methylindole,[3] 1-(4-bromophenyl)indole,[4] dihydro-3H-pyrrolo[1,2-α]indole,[5] 6,7,8,9-tetrahydropyrido[1,2-α]indole,[6] and 1,2-dimethyl-5-methoxyindole,[7] dirhodium tetrakis *N*-1,8-naphthoyl (*S*)-*tert*-leucinate,[8] dirhodium tetrakis *N*-phthaloyl (*S*)-*tert*-leucinate,[9] dirhodium tetrakis *N*-tetrachlorophthaloyl (*S*)-*tert*-leucinate,[10] dirhodium tetrapivalate,[11] 4-iodo-*N*-*tert*-butoxycarbonylamino-benzene,[12] and *tert*-butyl(4-iodophenoxy)dimethylsilane[13] were also prepared by literature methods. X-ray quality crystals of **G** were grown by slow diffusion of a solution of **G** in 1:1 benzene/hexanes into hexanes. Enantiomeric excesses were measured on materials directly after chromatography (i.e. the reported ee's have not been enhanced through crystallization).

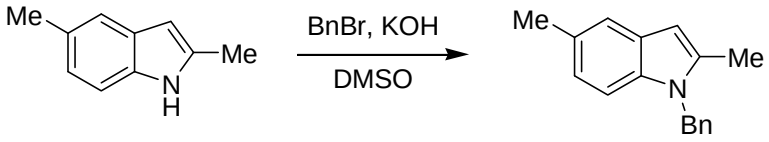
Assignment of Absolute Configuration

For the indole functionalization reactions catalyzed by Rh_2(*S*-NTTL)$_4$, the absolute configuration was determined by x-ray diffraction of compound **G** which was prepared from indole **C** and methyl 2-diazobutanoate. From the x-ray data, it was determined that the absolute configuration of the product is *R*.



Experimental Procedures

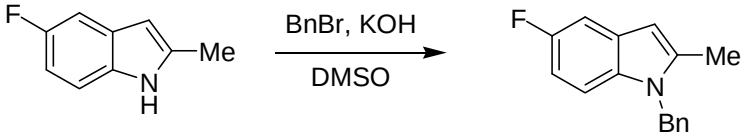
1-Benzyl-2,5-dimethylindole (A)



To a dry round bottomed flask was added 1.55 g powdered KOH (27.6 mmol) and 13.5 mL DMSO. The mixture was stirred at ambient temperature for 5 minutes and then 1.00 g (6.89 mmol) of 2,5-dimethylindole was added and the mixture was stirred for an additional 45 minutes and then cooled by an ice bath (0 °C). Benzyl bromide (1.65 mL, 13.8 mmol) was then added

and the mixture was allowed to warm to ambient temperature and stir for 45 minutes. It was then diluted with 13.5 mL of water and extracted with three 50 mL portions of Et_2O. The combined organic extracts were then washed with three 50 mL portions of water, dried over anhydrous $MgSO_4$, decanted, and concentrated. The residue was chromatographed on silica gel eluting with pure hexanes to give 0.545 g (2.32 mmol, 34%) of the title compound as a white solid, m.p. 73 – 75 °C. ^{1}H NMR (C_6D_6, 400 MHz, δ): 7.48 (s, 1H), 7.01 – 6.88 (m, 5H), 6.72 – 6.67 (m, 2H), 6.30 (s, 1H), 4.70 (s, 2H), 2.43 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 138.6 (u), 136.4 (u) (2 carbons), 129.3 (dn), 128.9 (u), 128.8 (u), 127.3 (dn), 126.1 (dn), 122.8 (dn), 120.3 (dn), 109.3 (dn), 100.7 (dn), 46.3 (u), 21.8 (dn), 12.5 (dn); IR (Thin film, cm^{-1}): 3029, 2920, 2861, 1604, 1580, 1555, 1485, 1453, 1440, 1354, 1329, 1298, 1175, 1161, 1029, 866, 789, 717; HRMS-CI (NH_3) m/z: [M+], calcd for $C_{17}H_{17}N$, 235.1361; found 235.1356.

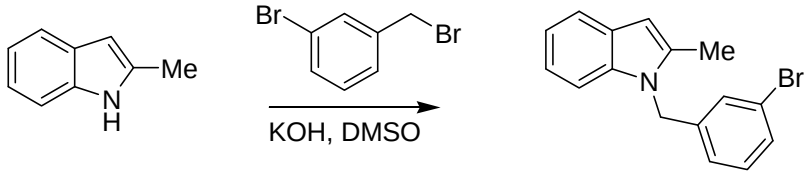
1-Benzyl-5-fluoro-2-methylindole (B)



To a dry round bottomed flask was added 1.50 g powdered KOH (26.8 mmol) and 13.5 mL DMSO. The mixture was stirred at ambient temperature for 5 minutes and then 1.00 g (6.71 mmol) of 5-fluoro-2-methylindole was added and the mixture was stirred for an additional 45 minutes and then cooled by an ice bath (0 °C). Benzyl bromide (1.60 mL, 13.4 mmol) was then added and the mixture was allowed to warm to ambient temperature and stir for 45 minutes. It was then diluted with 13.5 mL of water and extracted with three 50 mL portions of Et_2O. The combined organic extracts were then washed with three 50 mL portions of water, dried over

anhydrous $MgSO_4$, decanted, and concentrated. The residue was chromatographed on silica gel eluting with pure hexanes to give 0.855 g (3.58 mmol, 53%) of the title compound as a white solid, m.p. 72 – 74 °C. ^{1}H NMR (C_6D_6, 400 MHz, δ): 7.36 – 7.32 (m, 1H), 6.96 – 6.90 (m, 3H), 6.90 – 6.85 (m, 1H), 6.71 – 6.67 (m, 1H), 6.64 – 6.58 (m, 2H), 6.13 (s, 1H), 4.57 (s, 2H), 1.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 158.0 (u) [d, ^1J(CF) = 232 Hz], 138.5 (u), 137.5 (u), 133.6 (u), 128.8 (dn), 128.4 (u) [d, ^3J(CF) = 9.8 Hz], 127.4 (dn), 125.8 (dn), 109.7 (dn) [d, ^3J(CF) = 10 Hz], 108.8 (dn) [d, ^2J(CF) = 26 Hz], 104.6 (dn) [d, ^2J(CF) = 23 Hz], 100.5 (dn) [d, ^4J(CF) = 4.4 Hz], 46.6 (u), 12.9 (dn); IR (Thin film, cm^{-1}): 3064, 3032, 2921, 1620, 1587, 1483, 1451, 1402, 1355, 1334, 1181, 1144, 1123, 1104, 1029, 953, 859, 792; HRMS-CI (NH_3) m/z: [M+], calcd for $C_{16}H_{14}NF$, 239.1110; found 239.1107.

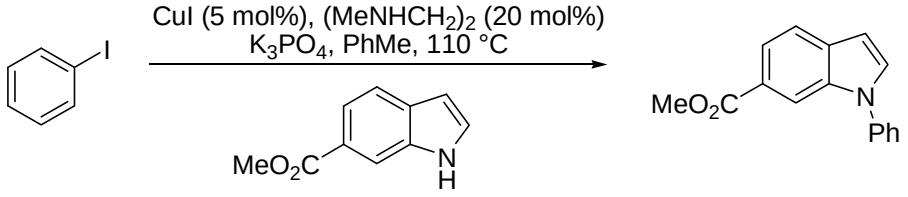
1-(3-Bromobenzyl)-2-methylindole (C)



To a dry round bottomed flask was added 8.55 g powdered KOH (152 mmol) and 76 mL DMSO. The mixture was stirred at ambient temperature for 5 minutes and then 5.00 g (38.1 mmol) of 2-methylindole was added and the mixture was stirred for an additional 45 minutes and then cooled by an ice bath (0 °C). 3-Bromobenzyl bromide (19.0 g, 76.2 mmol) was then added and the mixture was allowed to warm to ambient temperature and stir for 45 minutes. It was then diluted with 76 mL of water and extracted with three 150 mL portions of Et_2O. The combined organic extracts were then washed with three 50 mL portions of water, dried over anhydrous $MgSO_4$,

decanted, and concentrated. The residue was chromatographed on silica gel eluting with pure hexanes to give 5.64 g (18.8 mmol, 49%) of the title compound as a pale yellow oil. ^{1}H NMR (C_6D_6, 400 MHz, δ): 7.63 (d, J = 7.8 Hz, 1H), 7.19 – 7.08 (m, 2H), 7.03 – 6.96 (m, 2H), 6.90 (d, J = 8.2 Hz, 1H), 6.44 (app t, J = 8.0 Hz, 1H), 6.34 – 6.25 (m, 2H), 4.47 (s, 2H), 1.83 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 140.8 (u), 137.6 (u), 136.2 (u), 130.6 (dn), 130.5 (dn), 129.3 (dn), 128.9 (u), 124.5 (dn), 123.0 (u), 121.4 (dn), 120.4 (dn), 120.3 (dn), 109.3 (dn), 101.3 (dn), 45.4 (u), 12.4 (dn); IR ($CHCl_3$, cm^{-1}): 3053, 2937, 2861, 1596, 1571, 1555, 1476, 1463, 1427, 1398, 1336, 1310, 1257, 1166, 1071, 1009, 896, 776, 747; HRMS-CI (NH_3) m/z: [M+], calcd for $C_{16}H_{14}N^{79}Br$, 299.0310; found 299.0305.

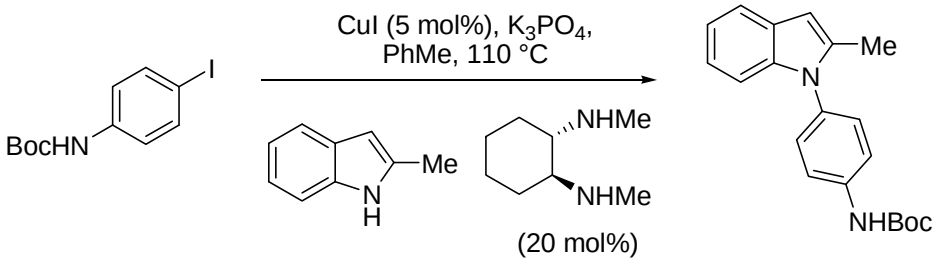
Methyl 1-phenyl-1*H*-indole-6-carboxylate (D)



A literature procedure was followed.[2] Thus, a resealable Schlenk tube was charged with CuI (24 mg, 0.13 mmol), indole-6-methoxycarbonyl (0.525 g, 3.0 mmol), and K_3PO_4 (1.11 g, 5.3 mmol) and the vessel was evacuated and filled with N_2. Iodobenzene (0.28 mL, 2.5 mmol), *N*,*N*'-dimethylethylenediamine (54 μL, 0.50 mmol), and toluene (2.5 mL) were then added and the vessel was sealed and heated to 110 °C for 20h. The reaction mixture was then allowed to cool to ambient temperature, diluted with 10 mL of ethyl acetate, filtered through a plug of silica eluting with 50 mL of additional ethyl acetate, concentrated, and chromatographed on silica gel eluting with a gradient of 0 – 10% ethyl acetate/hexanes to give 0.45 g (1.8 mmol, 72%) of **D** as a white

solid, m.p. 66 – 68 °C. The purity was measured to be > 95% by ^{1}H NMR. ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.59 – 8.58 (m, 1H), 8.24 (dd, *J* = 8.6 Hz, 1.6 Hz, 1H), 7.60 (dd, *J* = 8.3 Hz, 0.68 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.99 – 6.89 (m, 4H), 6.49 (dd, *J* = 3.3 Hz, 0.90 Hz, 1H), 3.52 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 167.7 (u), 139.3 (u), 135.9 (u), 133.4 (u), 131.1 (dn), 129.8 (dn), 126.9 (dn), 125.2 (u), 124.7 (dn), 122.2 (dn), 121.3 (dn), 113.2 (dn), 104.1 (dn), 51.5 (dn); IR ($CHCl_3$, cm^{-1}): 3012, 2953, 1710, 1599, 1507, 1449, 1345, 1289, 1249, 1216, 1143, 1086, 992, 696; HRMS-CI (NH_3) m/z: [M+H], calcd for $C_{16}H_{14}NO_2$, 252.1025; found 252.1021.

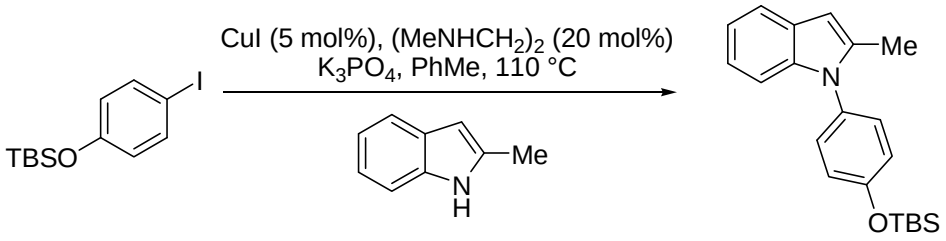
tert-Butyl 4-(2-methyl-1*H*-indol-1-yl)phenylcarbamate (E)



A literature procedure was followed.[2] Thus, a resealable Schlenk tube was charged with CuI (48 mg, 0.25 mmol), 2-methylindole (0.66 g, 5.0 mmol), and K_3PO_4 (2.23 g 10.5 mmol) and the vessel was evacuated and filled with N_2. *tert*-butyl 4-iodophenylcarbamate[12] (1.91 g, 6.00 mmol), *trans*-*N*,*N*'-dimethyl-1,2-cyclohexanediamine (0.16 mL, 1.0 mmol), and toluene (5 mL) were then added and the vessel was sealed and heated to 110 °C for 48h. The reaction mixture was then allowed to cool to ambient temperature, diluted with 20 mL of ethyl acetate, filtered through a plug of silica eluting with 100 mL of additional ethyl acetate, concentrated, and chromatographed on silica gel eluting with 50 % toluene/hexanes to give 0.23 g (0.71 mmol, 14%) of **E** as a white solid, m.p. 178 – 180 °C. The purity was measured to be > 95% by ^{1}H

NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.58 – 7.51 (m, 3H), 7.30 – 7.26 (2H), 7.12 – 7.05 (m, 3H), 6.62 (s, 1H), 6.39 (s, 1H), 2.29 (d, J = 0.89 Hz, 3H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 152.7 (u), 138.2 (u), 137.8 (u), 137.2 (u), 132.6 (u), 128.6 (dn), 128.0 (u), 120.9 (dn), 119.9 (dn), 119.5 (dn), 119.1 (dn), 109.9 (dn), 100.9 (dn), 80.9 (u), 28.3 (dn), 13.3 (dn); IR ($CHCl_3$, cm^{-1}): 3438, 3011, 2983, 1726, 1522, 1459, 1410, 1391, 1369, 1308, 1216, 1156, 1054; HRMS-ESI m/z: [M+H], calcd for $C_{20}H_{23}N_2O_2$, 323.1760; found 323.1753.

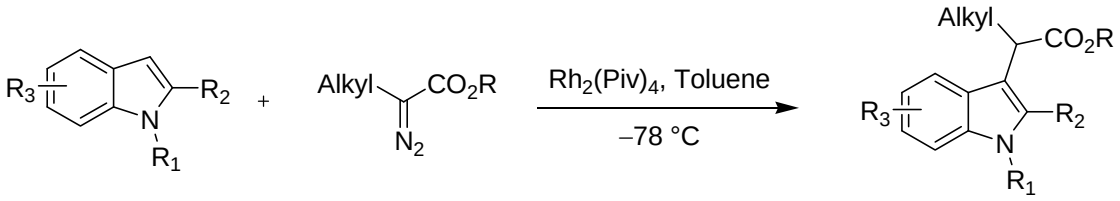
1-(4-(*tert*-Butyldimethylsilyloxy)phenyl)-2-methyl-1*H*-indole (F)



A literature procedure was followed.[2] Thus, a resealable Schlenk tube was charged with CuI (48 mg, 0.25 mmol), 2-methylindole (0.78 g, 6.0 mmol), and K_3PO_4 (2.23 g 10.5 mmol) and the vessel was evacuated and filled with N_2. *tert*-butyl(4-iodophenoxy)dimethylsilane[13] (1.67 g, 5.00 mmol), *N,N*'-dimethylethylenediamine (0.11 mL, 1.0 mmol), and toluene (5 mL) were then added and the vessel was sealed and heated to 110 °C for 48h. The reaction mixture was then allowed to cool to ambient temperature, diluted with 20 mL of ethyl acetate, filtered through a plug of silica eluting with 100 mL of additional ethyl acetate, concentrated, and chromatographed on silica gel eluting with hexanes to give 1.15 g (3.41 mmol, 68%) of **F** as a pale yellow oil. The purity was measured to be > 95% by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.59 – 7.54 (m, 1H), 7.23 – 7.18 (m, 2H), 7.13 – 7.06 (m, 3H), 7.01 – 6.96 (m, 2H), 6.39 (s,

1H), 2.31 (d, J = 1.0 Hz, 3H), 1.04 (s, 9H), 0.29 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 155.2 (u), 138.4 (u), 137.3 (u), 131.1 (u), 129.1 (dn), 128.0 (u), 120.8 (dn), 120.7 (dn), 119.8 (dn), 119.4 (dn), 110.0 (dn), 100.6 (dn), 25.6 (dn), 18.2 (u), 13.3 (dn), –4.39 (dn); IR ($CHCl_3$, cm^{-1}): 3008, 2957, 2932, 2860, 1609, 1511, 1460, 1391, 1323, 1265, 1163, 913.

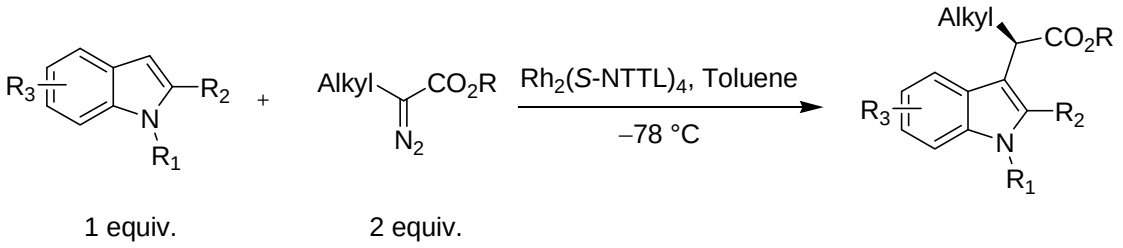
General procedure for the preparation of racemic samples



1 equiv. 2 equiv. +/-

In a dry round bottomed flask, Rh_2Piv_4 (1 mg, 0.002 mmol) and 0.40 mmol of indole were dissolved in anhydrous toluene (2.0 mL) and cooled by a bath of dry ice/acetone (−78 °C) under a nitrogen atmosphere. The appropriate diazoester (0.80 mmol) was dissolved in anhydrous toluene (1.2 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. After the addition was complete, the mixture was allowed to warm to ambient temperature. The solvent was subsequently removed and the residue was chromatographed on silica gel.

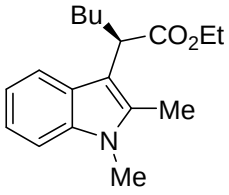
General Procedure for Enantioselective Indole Functionalization



1 equiv. 2 equiv.

A dry round bottomed flask was charged with 3 mg (0.002 mmol) of Rh_2(*S*-NTTL)$_4$ and 0.40 mmol of indole, and the flask was evacuated and filled with nitrogen. Anhydrous toluene (2.0 mL) was added, and the flask was cooled by a bath of dry ice/acetone (−78 °C). The appropriate diazoester (0.80 mmol) was dissolved in anhydrous toluene (1.2 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. After the addition was complete, the mixture was allowed to warm to ambient temperature. The solvent was subsequently removed and the residue was chromatographed on silica gel.

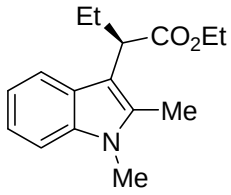
(*R*) -(−)-Ethyl 2-(1,2-dimethyl-1*H*-indol-3-yl)hexanoate (1)



The general procedure for enantioselective indole functionalization was followed on 1.5× scale: 87 mg (0.60 mmol) of 1,2-dimethylindole and 204 mg (1.20 mmol) of ethyl 2-diazohexanoate gave 167 mg (0.58 mmol, 97%) of **1** as a pale yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 94% by HPLC analysis. A similar

experiment starting with 58 mg (0.40 mmol) of 1,2-dimethylindole and 136 mg (0.80 mmol) of ethyl 2-diazohexanoate gave 108 mg (0.38 mmol, 95%) of **1**. The enantiomeric excess was measured to be 95% by HPLC analysis. $[\alpha]^{18}_{D} = -52.6°$ (*c*. 1.01 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.10 (app d, *J* = 8.3 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.01 – 6.96 (m, 1H), 4.06 – 3.98 (m, 1H), 3.97 – 3.86 (m, 2H), 2.78 (s, 3H), 2.50 – 2.39 (m, 1H), 2.22 – 2.10 (m, 1H), 2.06 (s, 3H), 1.42 – 1.18 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.3 (u), 137.3 (u), 133.5 (u), 127.3 (u), 121.1 (dn), 119.9 (dn), 119.6 (dn), 109.3 (u), 109.0 (dn), 60.4 (u), 43.5 (dn), 32.1 (u), 30.4 (u), 28.8 (dn), 23.0 (u), 14.3 (dn) (2 carbons), 10.4 (dn); IR ($CHCl_3$, cm^{-1}): 3007, 2958, 2933, 2872, 1724, 1612, 1562, 1471, 1369, 1335, 1216, 1173, 1116, 1039, 757; HRMS-CI (NH_3) m/z: [M+], calcd for $C_{18}H_{25}NO_2$, 287.1885; found 287.1883.

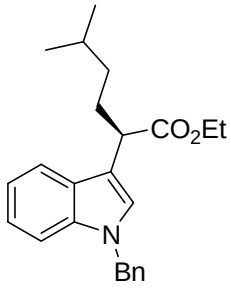
(*R*)-(–)-Ethyl 2-(1,2-dimethyl-1*H*-indol-3-yl)butanoate (2)



The general procedure for enantioselective indole functionalization was followed with 58 mg (0.40 mmol) of 1,2-dimethylindole and 114 mg (0.80 mmol) of ethyl 2-diazobutanoate to give 94 mg (0.36 mmol, 90%) of **2** as a pale yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 89% by HPLC analysis. An identical experiment gave 93 mg (0.36 mmol, 90%) of **2**. The enantiomeric excess was measured to be 91% by HPLC analysis. $[\alpha]^{18}_{D} = -46.1°$ (*c*. 1.01 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.08 –

7.99 (m, 1H), 7.22 – 7.16 (m, 2H), 7.01 – 6.94 (m, 1H), 4.03 – 3.95 (m, 1H), 3.94 – 3.86 (m, 1H), 3.78 – 3.69 (app t, J = 7.7 Hz, 1H), 2.80 (s, 3H), 2.48 – 2.36 (m, 1H), 2.15 – 2.05 (m, 1H), 2.00 (s, 3H), 0.94 – 0.84 (m, 6H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.2 (u), 137.3 (u), 133.6 (u), 127.2 (u), 121.1 (dn), 119.8 (dn), 119.6 (dn), 109.0 (u), 109.0 (dn), 60.3 (u), 45.2 (dn), 28.8 (dn), 25.4 (u), 14.3 (dn), 12.6 (dn), 10.3 (dn); IR ($CHCl_3$, cm^{-1}): 3006, 2969, 2935, 2875, 1723, 1612, 1561, 1472, 1369, 1336, 1251, 1191, 1114, 1022, 754; HRMS-CI (NH_3) m/z: [M+], calcd for $C_{16}H_{21}NO_2$, 259.1572; found 259.1560.

(*R*) -(–)-Ethyl 5-methyl-2-(1-benzyl-1*H*-indol-3-yl)hexanoate (3)

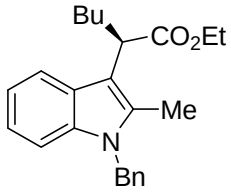


The general procedure for enantioselective indole functionalization was followed starting with 83 mg (0.40 mmol) of 1-benzylindole and 147 mg (0.80 mmol) of ethyl 2-diazo-5-methylhexanoate to give 133 mg (0.37 mmol, 93%) of **3** as a pale yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 84% by HPLC analysis. A similar experiment starting with 84 mg (0.41 mmol) of 1-benzylindole and 149 mg (0.80 mmol) of ethyl 2-diazo-5-methylhexanoate gave 141 mg (0.39 mmol, 95%) of **3**. The enantiomeric excess was measured to be 84% by HPLC analysis. $[\alpha]^{19}_D$ = –25.5° (*c*. 1.00 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.00 (d, J = 7.7 Hz, 1H), 7.22 – 7.12 (m, 2H), 7.03 (d, J = 8.6 Hz, 1H), 6.99 – 6.91 (m, 4H), 6.78 – 6.70 (m, 2H), 4.67 – 4.58 (m, 2H),[a] 4.07 – 3.89 (m,

3H), 2.40 – 2.29 (m, 1H), 2.08 – 1.97 (m, 1H), 1.53 – 1.45 (m, 1H), 1.40 – 1.20 (m, 2H), 0.90 (t, J = 7.0 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.5 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.4 (u), 138.1 (u), 137.3 (u), 128.8 (dn), 128.2 (u), 127.6 (dn), 126.8 (dn), 126.4 (dn), 122.4 (dn), 120.2 (dn), 119.9 (dn), 114.3 (u), 110.3 (dn), 60.5 (u), 49.8 (u), 43.8 (dn), 37.5 (u), 31.6 (u), 28.3 (dn), 22.8 (dn), 22.7 (dn), 14.3 (dn); IR ($CHCl_3$, cm^{-1}): 3019, 2958, 2871, 1724, 1468, 1369, 1335, 1224, 1208, 1176, 1030, 789, 669; HRMS-ESI m/z: [M+H], calcd for $C_{24}H_{30}NO_2$, 364.2277; found 364.2271.

[a]AB-spinsystem: δ_A=4.63 ppm, δ_B=4.61 ppm, J(AB)=17 Hz

(*R*) -(–)-Ethyl 2-(1-benzyl-2-methyl-1*H*-indol-3-yl)hexanoate (4)

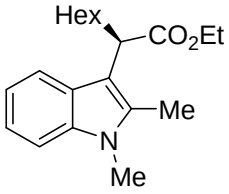


The general procedure for enantioselective indole functionalization was followed on 0.5× scale: 44 mg (0.20 mmol) of 1-benzyl-2-methylindole[3] and 68 mg (0.40 mmol) of ethyl 2-diazohexanoate gave 70 mg (0.19 mmol, 95%) of **4** as a yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 96% by HPLC analysis. A similar experiment starting with 88 mg (0.40 mmol) of 1-benzyl-2-methylindole and 136 mg (0.80 mmol) of ethyl 2-diazohexanoate gave 136 mg (0.37 mmol, 94%) of **4**. The enantiomeric excess was measured to be 95% by HPLC analysis. $[\alpha]^{18}_D$ = –44.3° (*c*. 1.06 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.15 (d, J = 8.3 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.14 – 7.09 (m, 1H), 7.00

(t, J = 8.0 Hz, 1H), 6.98 – 6.90 (m, 3H), 6.68 – 6.62 (m, 2H), 4.76 – 4.63 (m, 2H),[a] 4.03 – 3.85 (m, 3H), 2.52 – 2.40 (m, 1H), 2.25 – 2.13 (m, 1H), 2.08 (s, 3H), 1.40 – 1.18 (m, 4H), 0.87 (t, J = 7.3 Hz, 3H), 0.78 (t, J = 7.3 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.2 (u), 138.4 (u), 137.3 (u), 133.6 (u), 128.9 (dn), 127.5 (u), 127.3 (dn), 126.1 (dn), 121.6 (dn), 120.1 (dn), 120.0 (dn), 110.2 (u), 109.4 (dn), 60.4 (u), 46.3 (u), 43.5 (dn), 32.0 (u), 30.5 (u), 23.0 (u), 14.3 (dn) (2 carbons), 10.4 (dn); IR ($CHCl_3$, cm^{-1}): 3008, 2958, 2931, 2871, 1723, 1607, 1564, 1468, 1369, 1171, 1116, 1027, 740; HRMS-CI (NH_3) m/z: [M+], calcd for $C_{24}H_{29}NO_2$, 363.2198; found 363.2203.

[a]AB-spinsystem: δ_A=4.72 ppm, δ_B=4.67 ppm, J(AB)=18 Hz

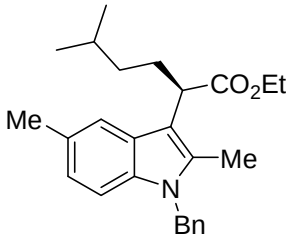
(*R*) -(–)-Ethyl 2-(1,2-dimethyl-1*H*-indol-3-yl)octanoate (5)



The general procedure for enantioselective indole functionalization was followed with 58 mg (0.40 mmol) of 1,2-dimethylindole and 238 mg (1.20 mmol) of ethyl 2-diazooctanoate to give 105 mg (0.33 mmol, 83%) of **5** as a yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 95% by HPLC analysis. An identical experiment gave 100 mg (0.32 mmol, 80%) of **5**. The enantiomeric excess was measured to be 96% by HPLC analysis. $[\alpha]^{18}_D$ = –52.6° (*c*. 1.06 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.10 – 8.04 (m, 1H), 7.22 – 7.15 (m, 2H), 6.98 – 6.94 (m, 1H), 4.06 – 3.97 (m, 1H), 3.96 – 3.86 (m,

2H), 2.80 (s, 3H), 2.49 – 2.37 (m, 1H), 2.22 – 2.11 (m, 1H), 2.09 (s, 3H), 1.40 – 1.10 (m, 8H), 0.89 (t, J = 7.0 Hz, 3H), 0.81 (t, J = 6.6 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.3 (u), 137.3 (u), 133.5 (u), 127.3 (u), 121.1 (dn), 119.9 (dn), 119.6 (dn), 109.3 (u), 109.0 (dn), 60.4 (u), 43.6 (dn), 32.4 (u), 32.2 (u), 29.7 (u), 28.8 (dn), 28.3 (u), 23.1 (u), 14.3 (dn) (2 carbons), 10.4 (dn); IR ($CHCl_3$, cm^{-1}): 3030, 3006, 2959, 2930, 2858, 1723, 1613, 1562, 1471, 1409, 1370, 1336, 1251, 1172, 1118, 1040; HRMS-CI (NH_3) m/z: [M+], calcd for $C_{20}H_{29}NO_2$, 315.2198; found 315.2187.

(*R*) -(–)-Ethyl 5-methyl-2-(1-benzyl-2,5-dimethyl-1*H*-indol-3-yl)hexanoate (6)

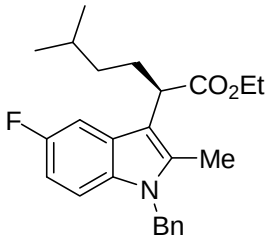


The general procedure for enantioselective indole functionalization was followed with 94 mg (0.40 mmol) of 1-benzyl-2,5-dimethylindole and 147 mg (0.80 mmol) of ethyl 2-diazo-5-methylhexanoate to give 148 mg (0.38 mmol, 95%) of **6** as a yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 97% by HPLC analysis. An identical experiment gave 139 mg (0.36 mmol, 90%) of **6**. The enantiomeric excess was measured to be 96% by HPLC analysis. $[\alpha]^{18}_D$ = –40.2° (*c*. 1.00 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 7.95 (s, 1H), 7.00 – 6.88 (m, 5H), 6.65 (d, J = 7.0 Hz, 2H), 4.78 – 4.65 (m, 2H),[a] 4.06 – 3.82 (m, 3H), 2.58 – 2.40 (m, 1H), 2.40 (s, 3H), 2.28 – 2.15 (m, 1H), 2.09 (s, 3H), 1.53 – 1.41 (m, 1H), 1.33 – 1.15 (m, 2H), 0.88 (t, J = 7.0 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H), 0.79

(d, J = 6.7 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.2 (u), 138.6 (u), 135.8 (u), 133.7 (u), 128.9 (dn), 128.8 (u), 127.7 (dn), 127.3 (dn), 126.0 (dn), 123.1 (dn), 119.8 (dn), 109.7 (u), 109.2 (dn), 60.4 (u), 46.3 (u), 43.7 (dn), 37.5 (u), 30.1 (u), 28.3 (dn), 22.9 (dn), 22.8 (dn), 21.9 (dn), 14.4 (dn), 10.5 (dn); IR ($CHCl_3$, cm^{-1}): 3030, 3006, 2956, 2870, 1723, 1581, 1454, 1416, 1370, 1301, 1254, 1178, 1030, 913, 865, 793, 724; HRMS-CI (NH_3) m/z: [M+], calcd for $C_{26}H_{33}NO_2$, 391.2511; found 391.2505.

[a]AB-spinsystem: δ_A=4.74 ppm, δ_B=4.68 ppm, J(AB)=17 Hz

(*R*) -(–)-Ethyl 5-methyl-2-(1-benzyl-5-fluoro-2-methyl-1*H*-indol-3-yl)hexanoate (7)

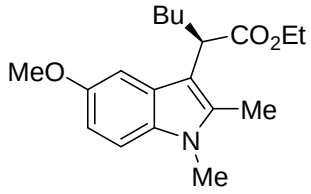


The general procedure for enantioselective indole functionalization was followed with 96 mg (0.40 mmol) of 1-benzyl-5-fluoro-2-methylindole and 147 mg (0.80 mmol) of ethyl 2-diazo-5-methylhexanoate to give 149 mg (0.38 mmol, 95%) of **7** as a yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 98% by HPLC analysis. An identical experiment gave 149 mg (0.38 mmol, 95%) of **7**. The enantiomeric excess was measured to be 97% by HPLC analysis. $[\alpha]^{18}_D$ = –37° (*c*. 0.95 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 7.95 (dd, J = 9.9 Hz, 2.2 Hz, 1H), 6.98 – 6.90 (m, 3H), 6.89 – 6.83 (m, 1H), 6.68 (dd, J = 8.8 Hz, 4.2 Hz, 1H), 6.61 – 6.57 (m, 2H), 4.64 – 4.53 (m, 2H),[a] 4.00 – 3.86 (m, 2H), 3.78 (app t, J = 7.7 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.14 – 2.03 (m, 1H), 2.00 (s, 3H), 1.49 –

1.41 (m, 1H), 1.27 – 1.08 (m, 2H), 0.87 (t, J = 7.1 Hz, 3H), 0.81 (d, J = 6.6 Hz, 3H), 0.77 (d, J = 6.6 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 173.9 (u), 158.6 (u) [d, ^1J(CF) = 233 Hz], 138.1 (u), 135.7 (u), 133.8 (u), 129.0 (dn), 127.7 (u) [d, ^3J(CF) = 10 Hz], 127.5 (dn), 125.9 (dn), 110.2 (u) [d, ^4J (CF) = 4.3 Hz], 110.1 (dn) [d, ^3J(CF) = 9.7 Hz], 109.6 (dn) [d, ^2J(CF) = 26 Hz], 105.3 (dn) [d, ^2J(CF) = 24 Hz], 60.5 (u), 46.5 (u), 43.7 (dn), 37.3 (u), 29.9 (u), 28.2 (dn), 22.8 (dn), 22.7 (dn), 14.3 (dn), 10.5 (dn); IR ($CHCl_3$, cm^{-1}): 3030, 2957, 2871, 1723, 1623, 1582, 1482, 1370, 1255, 1216, 1179, 1142, 1031, 915, 860, 768; HRMS-CI (NH_3) m/z: [M+], calcd for $C_{25}H_{30}NO_2F$, 395.2261; found 395.2260.

[a]AB-spinsystem: δ_A=4.61 ppm, δ_B=4.57 ppm, J(AB)=17 Hz

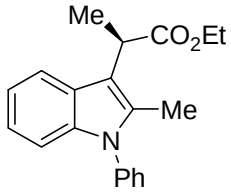
(*R*) -(–)-Ethyl 2-(1-benzyl-5-methoxy-2-methyl-1*H*-indol-3-yl)hexanoate (8)



The general procedure for enantioselective indole functionalization was followed with 70 mg (0.40 mmol) of 1-benzyl-5-methoxy-2-methylindole[7] and 136 mg (0.80 mmol) of ethyl 2-diazohexanoate to give 117 mg (0.37 mmol, 93%) of **8** as a pale yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 84% by HPLC analysis. An identical experiment gave 118 mg (0.37 mmol, 93%) of **8**. The enantiomeric excess was measured to be 83% by HPLC analysis. $[\alpha]^{19}_D$ = –38.5° (*c*. 1.00 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 7.63 (d, J = 2.7 Hz, 1H), 7.07 (dd, J = 8.9 Hz, 2.7 Hz, 1H), 6.85 (d, J = 8.9

Hz, 1H), 4.06 – 3.98 (m, 1H), 3.97 – 3.85 (m, 2H), 3.65 (s, 3H), 2.73 (s, 3H), 2.48 – 2.38 (m, 1H), 2.23 – 2.12 (m, 1H), 2.05 (s, 3H), 1.39 – 1.21 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H), 0.79 (t, J = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.3 (u), 154.8 (u), 134.0 (u), 132.5 (u), 127.5 (u), 111.3 (dn), 109.6 (dn), 108.9 (u), 101.9 (dn), 60.4 (u), 55.4 (dn), 43.6 (dn), 31.9 (u), 30.4 (u), 28.9 (dn), 23.1 (u), 14.4 (dn), 14.3 (dn), 10.5 (dn); IR ($CHCl_3$, cm^{-1}): 3018, 2958, 1722, 1488, 1456, 1411, 1371, 1216, 1179, 1155, 1031, 759, 668; HRMS-ESI m/z: [M+H], calcd for $C_{19}H_{28}NO_3$, 318.2056; found 318.2062.

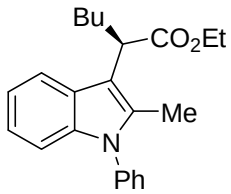
(*R*) -(–)-Ethyl 2-(2-methyl-1-phenyl-1*H*-indol-3-yl)propanoate (9)



The general procedure for enantioselective indole functionalization was followed with 81 mg (0.39 mmol) of 2-methyl-1-phenylindole[3] and 272 mg (2.13 mmol) of ethyl 2-diazopropanoate to give 94 mg (0.31 mmol, 79%) of **9** as a colorless oil. The purity was measured to be 94% by ^{1}H NMR. The enantiomeric excess was measured to be 79% by HPLC analysis. A similar experiment starting with 88 mg (0.43 mmol) of 2-methyl-1-phenylindole and 272 mg (2.13 mmol) of ethyl 2-diazopropanoate gave 111 mg (0.36 mmol, 84%) of **9**. The enantiomeric excess was measured to be 79% by HPLC analysis. $[\alpha]^{19}_D = -61°$ (*c*. 0.87 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.05 (d, J = 8.0 Hz, 1H), 7.20 (app t, J = 7.0 Hz, 1H), 7.13 – 7.00 (m, 2H), 7.00 – 6.93 (m, 3H), 6.88 – 6.73 (m, 2H), 4.06 – 3.97 (m, 2H), 3.97 – 3.87 (m, 1H), 2.07 (s, 3H), 1.74 (d, J = 7.4 Hz, 3H), 0.88 (t, J = 7.7 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.6 (u),

138.3 (u) (2 carbons), 133.1 (u), 129.5 (dn), 128.5 (dn), 127.6 (dn), 127.3 (u), 121.9 (dn), 120.5 (dn), 119.6 (dn), 112.6 (u), 110.5 (dn), 60.6 (u), 37.4 (dn), 17.9 (dn), 14.3 (dn), 11.1 (dn); IR ($CHCl_3$, cm^{-1}): 3019, 2983, 1723, 1598, 1501, 1461, 1370, 1325, 1216, 1093, 774, 700, 669; HRMS-ESI m/z: [M+H], calcd for $C_{20}H_{22}NO_2$, 308.1651; found 308.1644.

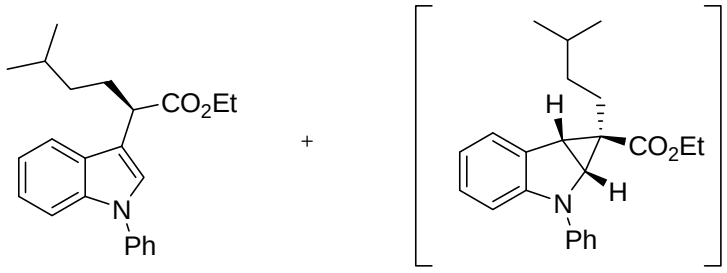
(*R*) -(–)-Ethyl 2-(2-methyl-1-phenyl-1*H*-indol-3-yl)hexanoate (10)



The general procedure for enantioselective indole functionalization was followed with 82 mg (0.40 mmol) of 2-methyl-1-phenylindole[3] and 135 mg (0.80 mmol) of ethyl 2-diazohexanoate to give 134 mg (0.38 mmol, 95%) of **10** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 98% by HPLC analysis. A similar experiment starting with 84 mg (0.41 mmol) of 2-methyl-1-phenylindole and 138 mg (0.81 mmol) of ethyl 2-diazohexanoate gave 136 mg (0.39 mmol, 95%) of **10**. The enantiomeric excess was measured to be 99% by HPLC analysis. $[\alpha]^{19}_D = -64.2°$ (*c*. 1.00 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.18 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.15 – 7.03 (m, 2H), 7.02 – 6.93 (m, 3H), 6.90 – 6.75 (m, 2H), 4.10 – 4.00 (m, 1H), 3.99 – 3.87 (m, 2H), 2.57 – 2.45 (m, 1H), 2.26 – 2.15 (m, 1H), 2.15 (s, 3H), 1.42 – 1.22 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.1 (u), 138.4 (u), 133.8 (u), 129.5 (dn), 128.5 (dn), 128.4 (u), 127.7 (u), 127.6 (dn), 121.9 (dn), 120.6 (dn), 120.1 (dn), 111.1 (u), 110.5 (dn), 60.5 (u), 43.7 (dn), 32.1 (u), 30.6 (u), 23.1 (u), 14.4 (dn), 14.3 (dn), 11.4 (dn); IR ($CHCl_3$, cm^{-1}):

3019, 2960, 1723, 1501, 1461, 1370, 1216, 1180, 762, 700, 669; HRMS-ESI m/z: [M+Na], calcd for $C_{23}H_{27}NO_2Na$, 372.1939; found 372.1935.

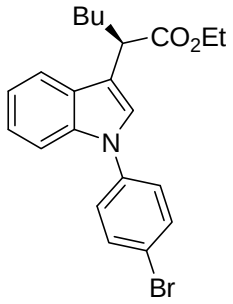
(*R*) -(–)-Ethyl 5-methyl-2-(1-phenyl-1*H*-indol-3-yl)hexanoate (11)



The general procedure for enantioselective indole functionalization was followed with 74 mg (0.38 mmol) of 1-phenylindole[2] and 141 mg (0.77 mmol) of ethyl 2-diazo-5-methylhexanoate to give 112 mg (0.32 mmol, 84%) of **11** which contained < 5% of the product of cyclopropanation as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 97% by HPLC analysis. A similar experiment starting with 81 mg (0.42 mmol) of 1-phenylindole and 155 mg (0.84 mmol) of ethyl 2-diazo-5-methylhexanoate gave 121 mg (0.37 mmol, 88%) of **11**. The enantiomeric excess was measured to be 98% by HPLC analysis. $[\alpha]^{19}_D = -25°$ (*c*. 0.92 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.02 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.18 – 7.15 (m, 1H), 7.08 – 6.97 (m, 4H), 6.95 – 6.89 (m, 1H), 4.07 – 3.90 (m, 3H), 2.46 – 2.36 (m, 1H), 2.11 – 2.00 (m, 1H), 1.58 – 1.47 (m, 1H), 1.42 – 1.28 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.2 (u), 140.0 (u), 136.7 (u), 129.7 (dn), 128.9 (u), 126.3 (dn), 126.0 (dn), 124.5 (dn), 123.1 (dn), 120.8 (dn), 120.3 (dn), 116.3 (u), 111.1(dn), 60.6 (u), 43.8 (dn), 37.5 (u), 31.5 (u), 28.4 (dn), 22.8 (dn), 22.7 (dn), 14.3 (dn); IR ($CHCl_3$, cm^{-1}): 3019,

2958, 1725, 1598, 1502, 1458, 1379, 1216, 1179, 1138, 748, 669; HRMS-ESI m/z: [M+H], calcd for $C_{23}H_{28}NO_2$, 350.2120; found 350.2111.

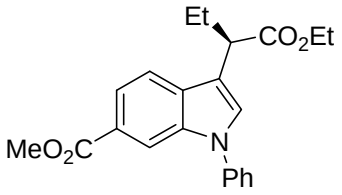
(*R*) -(–)-Ethyl 2-(1-(4-bromophenyl)-1*H*-indol-3-yl)hexanoate (12)



The general procedure for enantioselective indole functionalization was followed with 106 mg (0.39 mmol) of 1-(4-bromophenyl)indole[4] and 133 mg (0.78 mmol) of ethyl 2-diazohexanoate to give 157 mg (0.38 mmol, 97%) of **12** as a colorless oil. The purity was measured to be 95% by ^{1}H NMR. The enantiomeric excess was measured to be 91% by HPLC analysis. A similar experiment starting with 107 mg (0.39 mmol) of 1-(4-bromophenyl)indole and 134 mg (0.78 mmol) of ethyl 2-diazohexanoate gave 148 mg (0.36 mmol, 92%) of **12**. The enantiomeric excess was measured to be 89% by HPLC analysis. $[\alpha]^{19}_D = -13.7°$ (*c*. 1.00 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 7.98 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.16 – 7.08 (m, 4H), 6.64 (d, *J* = 9.4 Hz, 2H), 4.10 – 3.97 (m, 2H), 3.97 – 3.89 (m, 1H), 2.42 – 2.28 (m, 1H), 2.07 – 1.96 (m, 1H), 1.46 – 1.23 (m, 4H), 0.93 (t, *J* = 7.6 Hz, 3H), 0.82 (t, *J* = 7.6 Hz, 3H) (minor impurities detected at 7.33 ppm, 6.91 ppm, 6.86 ppm, 4.22 ppm, 3.23 ppm, 1.08 ppm, 0.70 ppm, and 0.60 ppm); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.1 (u), 138.8 (u), 136.4 (u), 132.7 (dn), 128.9 (u), 125.9 (dn), 125.6 (dn), 123.3 (dn), 121.0 (dn), 120.4 (dn), 119.6 (u), 116.6

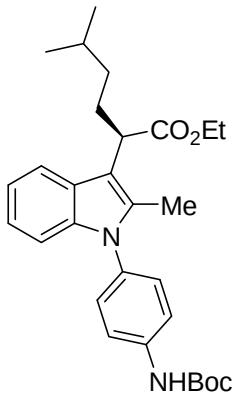
(u), 110.9 (dn), 60.7 (u), 43.4 (dn), 33.4 (u), 30.5 (u), 23.0 (u), 14.3 (dn), 14.1 (dn); IR ($CHCl_3$, cm^{-1}): 3019, 2960, 2932, 1725, 1591, 1494, 1458, 1380, 1215, 1178, 1072, 1012, 832, 760, 669; HRMS-ESI m/z: [M+H], calcd for $C_{22}H_{25}NO_2{}^{79}Br$, 414.1069; found 414.1061.

(*R*)-(–)-Methyl 3-(1-ethoxy-1-oxobutan-2-yl)-1-phenyl-1*H*-indole-6-carboxylate (13)



The general procedure for enantioselective indole functionalization was followed with 126 mg (0.50 mmol) of methyl 1-phenyl-1*H*-indole-6-carboxylate and 142 mg (1.00 mmol) of ethyl 2-diazobutanoate to give 158 mg (0.43 mmol, 86%) of **13** as a yellow oil. The purity was measured to be > 95% by ^{1}H NMR. The enantiomeric excess was measured to be 87% by HPLC analysis. An identical experiment gave 155 mg (0.42 mmol, 84%) of **13**. The enantiomeric excess was measured to be 88% by HPLC analysis. $[\alpha]^{22}_D = -20.8°$ (*c*. 1.00 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.56 (s, 1H), 8.28 (dd, *J* = 8.4 Hz, 1.5 Hz, 1H), 7.89 (dd, *J* = 8.41 Hz, 0.39 Hz, 1H), 7.28 (s, 1H), 7.02 – 6.87 (m, 5H), 4.03 – 3.88 (m, 2H), 3.84 (dd, *J* = 8.5 Hz, 6.8 Hz, 1H), 3.52 (s, 3H), 2.32 – 2.20 (m, 1H), 1.98 – 1.86 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 173.8 (u), 167.6 (u), 139.2 (u), 136.1 (u), 132.1 (u), 129.8 (dn), 129.2 (dn), 126.8 (dn), 125.4 (u), 124.6 (dn), 121.9 (dn), 120.0 (dn), 116.1 (u), 113.4 (dn), 60.7 (u), 51.6 (dn), 44.9 (dn), 26.7 (u), 14.3 (dn), 12.5 (dn); IR ($CHCl_3$, cm^{-1}): 3028, 2967, 2876, 1724, 1713, 1599, 1502, 1448, 1384, 1301, 1248, 1216, 1180, 1022, 697; HRMS-ESI m/z: [M+Na], calcd for $C_{22}H_{23}NO_4Na$, 388.1525; found 388.1507.

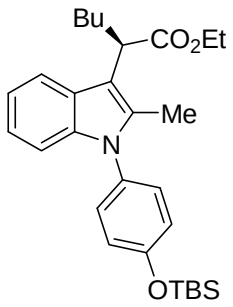
(*R*)-(–)-Ethyl 2-(1-(4-(*tert*-butoxycarbonyl)phenyl)-2-methyl-1*H*-indol-3-yl)-5-methylhexanoate (14)



The general procedure for enantioselective indole functionalization was followed with 63 mg (0.20 mmol) of *tert*-butyl 4-(2-methyl-1*H*-indol-1-yl)phenylcarbamate and 180 mg (1.0 mmol) of ethyl 2-diazo-5-methylhexanoate to give 80 mg (0.17 mmol, 85%) of **14** as a white solid, m.p. 63 – 67 °C. The purity was measured to be > 95% by ^{1}H NMR. The enantiomeric excess was measured to be 97% by HPLC analysis. A similar experiment starting with 62 mg (0.19 mmol) of *tert*-butyl 4-(2-methyl-1*H*-indol-1-yl)phenylcarbamate and 177 mg (0.96 mmol) of ethyl 2-diazo-5-methylhexanoate gave 80 mg (0.17 mmol, 89%) of **14**. The enantiomeric excess was measured to be 96% by HPLC analysis. $[\alpha]^{22}_{D} = -49.3°$ (*c*. 1.00 $CHCl_3$); ^{1}H NMR (CD_2Cl_2, 400 MHz, δ): 7.73 – 7.69 (m, 1H), 7.57 – 7.53 (m, 2H), 7.28 – 7.23 (m, 2H), 7.08 – 7.01 (m, 3H), 6.80 (s, 1H), 4.20 – 4.11 (m, 1H), 4.10 – 4.01 (m, 1H), 3.80 (app t, *J* = 7.6 Hz, 1H), 2.33 – 2.23 (m, 1H), 2.24 (s, 3H), 2.02 – 1.90 (m, 1H), 1.61 – 1.53 (m, 1H), 1.54 (s, 9H), 1.28 – 1.12 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (CD_2Cl_2, 100 MHz, δ): 174.6 (u), 152.9 (u), 138.6 (u), 138.1 (u), 134.7 (u), 132.7 (u), 129.1 (dn), 127.1 (u), 121.3 (dn), 119.8 (dn), 119.6 (dn), 119.3 (dn), 110.2 (u), 110.1 (dn), 81.0 (u), 60.8 (u), 43.7 (dn), 37.3 (u), 29.8 (u), 28.4 (dn), 22.8 (dn, 2 carbons [signals resolved in C_6D_6]), 22.6 (dn),

14.4 (dn), 11.3 (dn); IR ($CHCl_3$, cm^{-1}): 3437, 3349 (br), 3009, 2958, 2871, 1724, 1594, 1522, 1462, 1410, 1369, 1309, 1230, 1157, 1054, 1018; HRMS-ESI m/z: [M+Na], calcd for $C_{29}H_{38}N_2O_4Na$, 501.2729; found 501.2723.

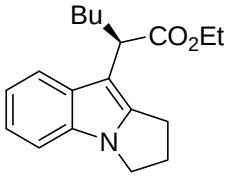
(R)-(–)-Ethyl 2-(1-(4-(*tert*-butyldimethylsilyloxy)phenyl)-2-methyl-1*H*-indol-3-yl)hexanoate (15)



The general procedure for enantioselective indole functionalization was followed with 134 mg (0.40 mmol) of 1-(4-(*tert*-butyldimethylsilyloxy)phenyl)-2-methyl-1*H*-indole and 135 mg (0.80 mmol) of ethyl 2-diazohexanoate to give 172 mg (0.36 mmol, 90%) of **15** as a pale yellow oil. The purity was measured to be 90% by ^{1}H NMR. The enantiomeric excess was measured to be 87% by HPLC analysis. A similar experiment starting with 127 mg (0.38 mmol) of 1-(4-(*tert*-butyldimethylsilyloxy)phenyl)-2-methyl-1*H*-indole and 128 mg (0.76 mmol) of ethyl 2-diazohexanoate gave 170 mg (0.35 mmol, 92%) of **15**. The enantiomeric excess was measured to be 85% by HPLC analysis. $[\alpha]^{22}_D$ = –40.0° (*c*. 1.00 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.79 – 7.76 (m, 1H), 7.19 (app d, *J* = 8.6 Hz, 2H), 7.12 – 7.01 (m, 3H), 6.97 (app d, *J* = 8.9 Hz, 2H), 4.23 – 4.15 (m, 1H), 4.13 – 4.04 (m, 1H), 3.82 (app t, *J* = 8.0 Hz, 1H), 2.35 – 2.25 (m, 1H), 2.26 (s, 3H), 2.05 – 1.92 (m, 1H), 1.40 – 1.26 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.04 (s, 9H), 0.88

(t, J = 7.0 Hz, 3H), 0.28 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 174.5 (u), 155.2 (u), 137.8 (u), 134.4 (u), 131.1 (u), 129.4 (dn), 126.7 (u), 120.8 (dn), 120.6 (dn), 119.4 (dn), 119.3 (dn), 109.9 (dn), 109.7 (u), 60.4 (u), 43.3 (dn), 31.4 (u), 30.1 (u), 25.6 (dn), 22.6 (u), 18.2 (u), 14.3 (dn), 14.0 (dn), 11.2 (dn), –4.39 (dn); IR ($CHCl_3$, cm^{-1}): 3008, 2959, 2932, 2861, 1723, 1609, 1512, 1463, 1179, 1163, 1117, 1098, 1022, 914, 844; HRMS-ESI m/z: [M+H], calcd for $C_{29}H_{42}NO_3Si$, 480.2934; found 480.2929.

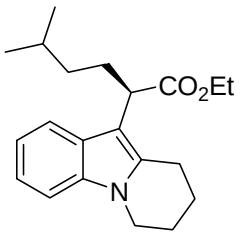
(*R*) -(–)-Ethyl 2-(2,3-dihydropyrrolo[1,2-a]indol-9-yl)hexanoate (16)



A dry round bottomed flask was charged with 3 mg (0.002 mmol) of Rh_2(*S*-NTTL)$_4$ and 63 mg (0.40 mmol) of dihydro-3H-pyrrolo[1,2-α]indole,[5] and the flask was evacuated and filled with nitrogen. Anhydrous toluene (2.0 mL) was added and the flask was cooled by a bath of dry ice/acetone (−78 °C). Ethyl 2-diazohexanoate (68 mg, 0.40 mmol) was dissolved in anhydrous toluene (1.2 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. After the addition was complete, the mixture was allowed to warm to ambient temperature. The solvent was subsequently evaporated and the residue was chromatographed on silica gel to give 97 mg (0.32 mmol, 80%) of **16** as a yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 95% by HPLC analysis. A similar experiment starting with 65 mg (0.41 mmol) of dihydro-3H-pyrrolo[1,2-α]indole and 70 mg (0.41 mmol) of ethyl 2-diazohexanoate gave 105 mg (0.35 mmol, 85%) of **16**. The enantiomeric

excess was measured to be 94% by HPLC analysis. $[\alpha]^{19}_{D} = -43°$ (*c*. 0.98 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 7.97 (app d, *J* = 7.3 Hz, 1H), 7.28 – 7.18 (m, 2H), 7.03 (app d, *J* = 8.0 Hz, 1H), 4.08 – 3.99 (m, 2H), 3.97 – 3.88 (m, 1H), 3.21 – 3.12 (m, 2H), 2.90 – 2.80 (m, 1H), 2.75 – 2.65 (m, 1H), 2.43 – 2.32 (m, 1H), 2.11 – 2.00 (m, 1H), 1.80 – 1.72 (m, 2H), 1.48 – 1.22 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.4 (u), 141.7 (u), 133.1 (u), 132.7 (u), 120.8 (dn), 119.6 (dn), 119.5 (dn), 109.7 (dn), 104.1 (u), 60.3 (u), 43.2 (dn), 43.0 (u), 32.4 (u), 30.5 (u), 27.4 (u), 24.4 (u), 23.1 (u), 14.4 (dn), 14.3 (dn); IR ($CHCl_3$, cm^{-1}): 3019, 2959, 2874, 1722, 1479, 1461, 1376, 1299, 1216, 1180, 1033, 740, 669; HRMS-CI (NH_3) m/z: [M+H], calcd for $C_{19}H_{26}NO_2$, 300.1964; found 300.1959.

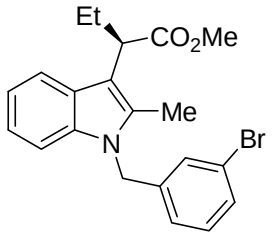
(*R*) -(–)-Ethyl 5-methyl-2-(6,7,8,9-tetrahydropyrido[1,2-a]indol-10-yl)hexanoate (17)



A dry round bottomed flask was charged with 3 mg Rh_2(*S*-NTTL)$_4$ and 73 mg (0.43 mmol) of 6,7,8,9-tetrahydropyrido[1,2-α]indole,[6] and the flask was evacuated and filled with nitrogen. Anhydrous toluene (2.0 mL) was added and the flask was cooled by a bath of dry ice/acetone (–78 °C). Ethyl 2-diazo-5-methylhexanoate (73 mg, 0.43 mmol) was dissolved in 1.2 mL of anhydrous toluene and the solution was added to the reaction mixture at a rate of 1 mL/hr. After addition was complete the reaction mixture was allowed to warm to ambient temperature. The solvent was subsequently evaporated and the residue was chromatographed on silica gel to give

94 mg (0.29 mmol, 67%) of **17** as a pale yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 95% by HPLC analysis. A similar experiment starting with 74 mg (0.43 mmol) of 6,7,8,9-tetrahydropyrido[1,2-α]indole and 80 mg (0.43 mmol) of ethyl 2-diazo-5-methylhexanoate gave 100 mg (0.31 mmol, 72%) of **17**. The enantiomeric excess was measured to be 95% by HPLC analysis. $[\alpha]^{19}_{D} = -50°$ (*c*. 0.71 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.16 (app d, *J* = 7.8 Hz, 1H), 7.30 – 7.20 (m, 2H), 7.05 (app d, *J* = 7.5 Hz, 1H), 4.08 – 3.97 (m, 1H), 3.95 – 3.84 (m, 2H), 3.32 – 3.20 (m, 2H), 2.85 – 2.72 (m, 2H), 2.53 – 2.44 (m, 1H), 2.23 – 2.14 (m, 1H), 1.57 – 1.45 (m, 1H), 1.39 – 1.20 (m, 6H), 1.97 – 1.82 (m, 6H), 0.79 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.2 (u), 136.8 (u), 133.7 (u), 127.5 (u), 120.8 (dn), 120.0 (dn), 119.9 (dn), 109.0 (dn), 107.8 (u), 60.4 (u), 43.4 (dn), 41.9 (u), 37.5 (u), 30.1 (u), 28.4 (dn), 23.1 (u), 23.0 (u), 22.9 (dn), 22.7 (dn), 21.1 (u), 14.4 (dn); IR ($CHCl_3$, cm^{-1}): 3019, 2956, 2871, 1722, 1462, 1422, 1367, 1330, 1317, 1216, 1175, 1163, 1117, 1034, 750, 669; HRMS-CI (NH_3) m/z: [M+H], calcd for $C_{21}H_{30}NO_2$, 328.2277; found 328.2274.

(*R*) -(–)-Methyl 2-(1-(3-bromobenzyl)-2-methyl-1*H*-indol-3-yl)butanoate (G)



General procedure I was followed with 120 mg (0.40 mmol) of 1-(3-bromobenzyl)-2-methylindole and 96 mg (0.75 mmol) of methyl 2-diazobutanoate to give 141 mg (0.35 mmol, 88%) of **G** as a white solid, m.p. 102 – 103 °C. The purity was measured to be ≥ 95% by ^{1}H

NMR. The enantiomeric excess was measured to be 88% by HPLC analysis. $[\alpha]^{18}_{D} = -49°$ (*c*. 0.98 $CHCl_3$); ^{1}H NMR (C_6D_6, 400 MHz, δ): 8.03 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.04 (m, 2H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.94 (s, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.44 (t, *J* = 8.1 Hz, 1H), 6.28 (d, *J* = 7.6 Hz, 1H), 4.53 – 4.41 (m, 2H),[a] 3.69 (dd, *J* = 9.0 Hz, 7.2 Hz, 1H), 3.30 (s, 3H), 2.44 – 2.33 (m, 1H), 2.18 – 2.06 (m, 1H), 1.91 (s, 3H), 0.84 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz, δ): 174.4 (u), 140.8 (u), 137.1 (u), 133.5 (u), 130.6 (dn), 130.5 (dn), 129.3 (dn), 127.4 (u), 124.4 (dn), 123.1 (u), 121.8 (dn), 120.3 (dn), 120.1 (dn), 110.0 (u), 109.2 (dn), 51.3 (dn), 45.6 (u), 44.8 (dn), 25.3 (u), 12.5 (dn), 10.2 (dn); IR (Thin film, cm^{-1}): 3050, 2964, 2873, 1732, 1596, 1571, 1468, 1429, 1337, 1197, 1167, 1003, 772, 742; HRMS-ESI m/z: [M+H], calcd for $C_{21}H_{23}NO_2{}^{79}Br$, 400.0912; found 400.0907.

[a]AB-spinsystem: δ_A=4.49 ppm, δ_B=4.45 ppm, *J*(AB)=18 Hz

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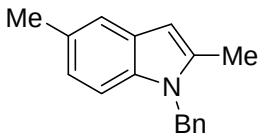
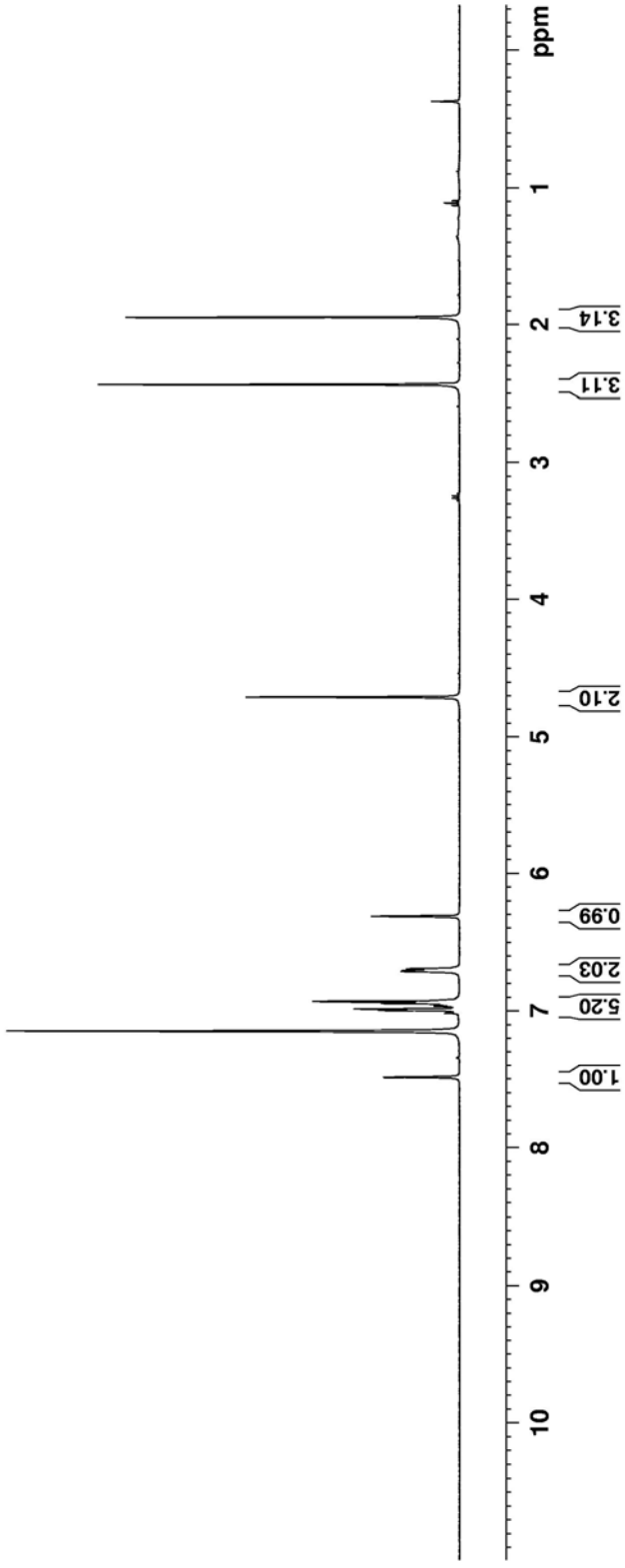
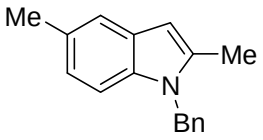
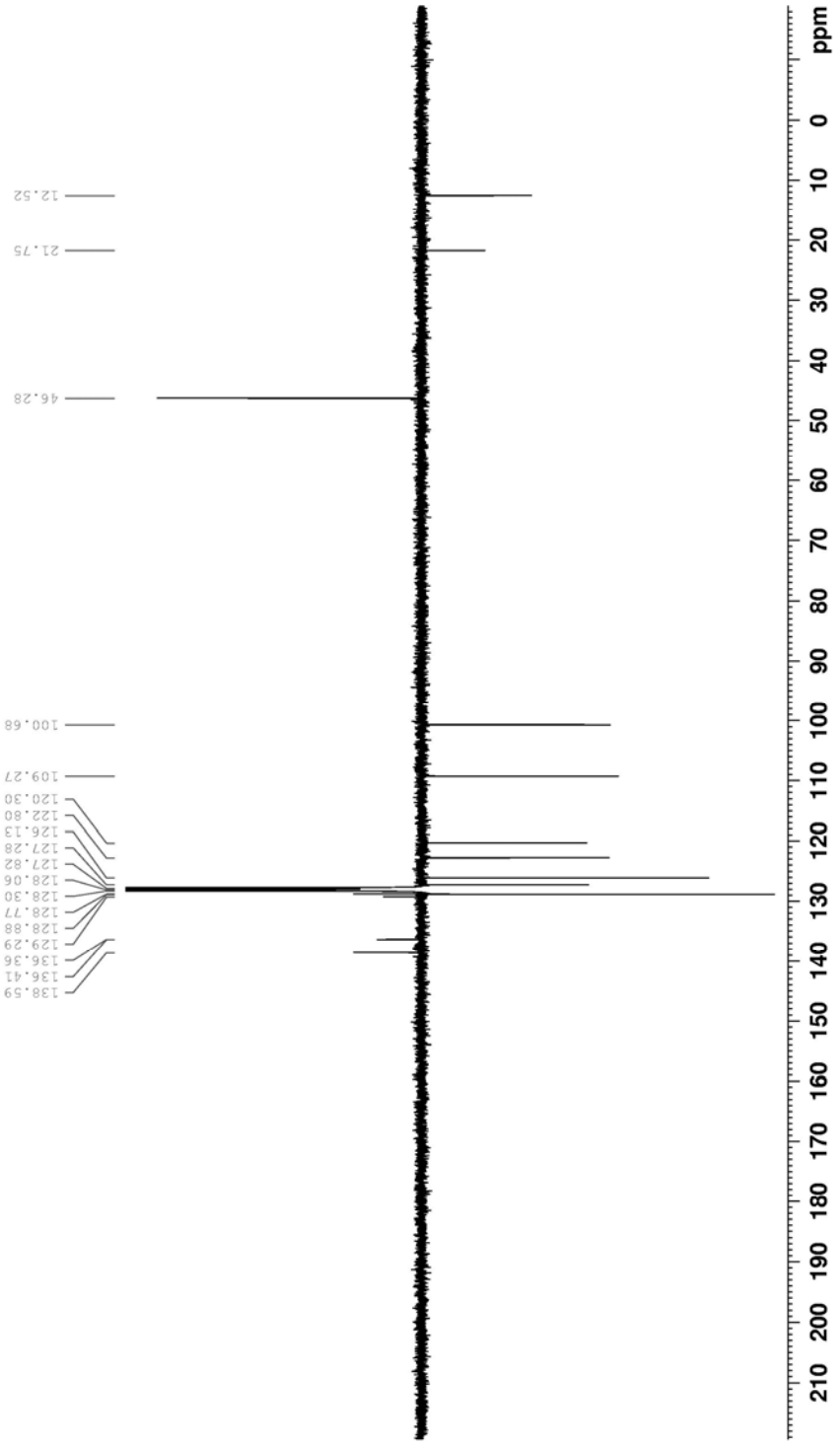
^{1}H NMR of A (400 MHz, C_6D_6)



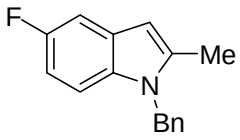


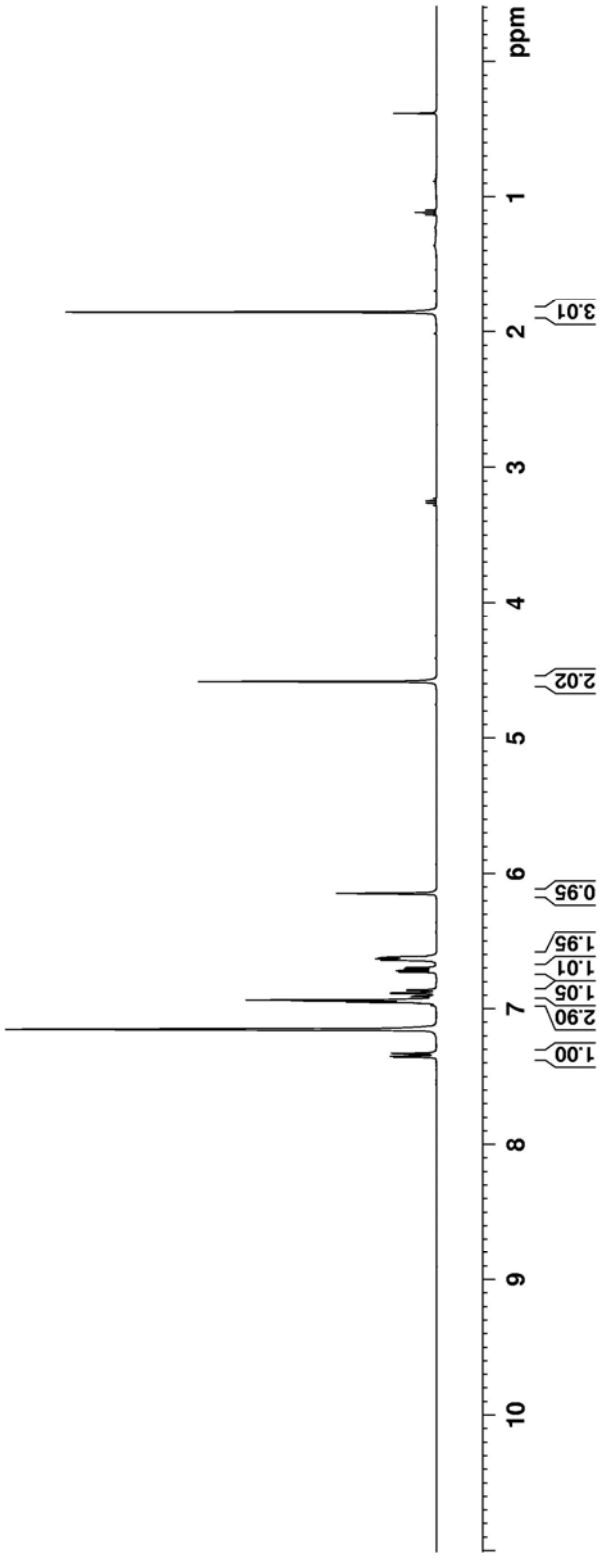
^{13}C NMR spectrum of A (100 MHz, C_6D_6)



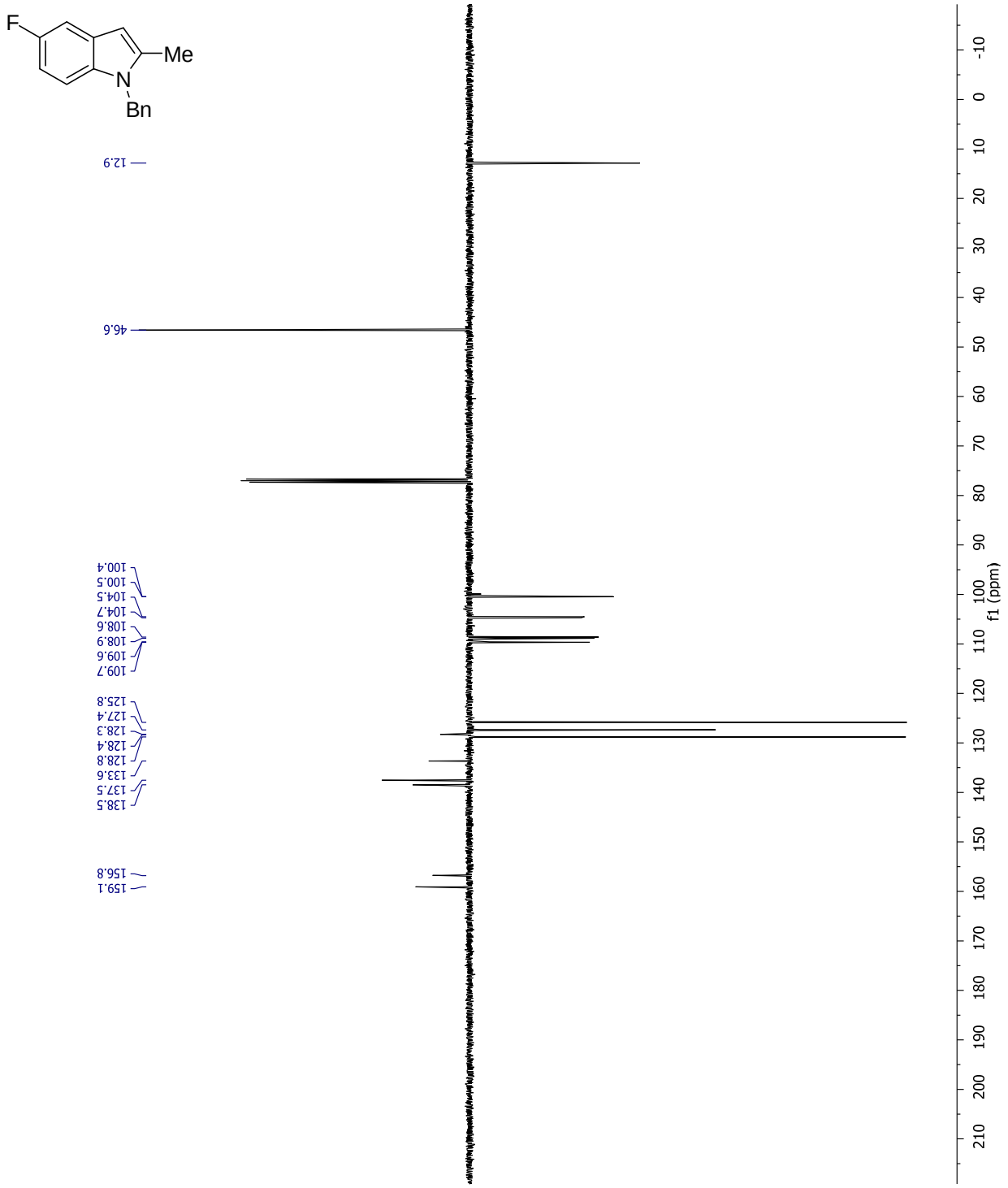


^{1}H NMR of B (400 MHz, C_6D_6)

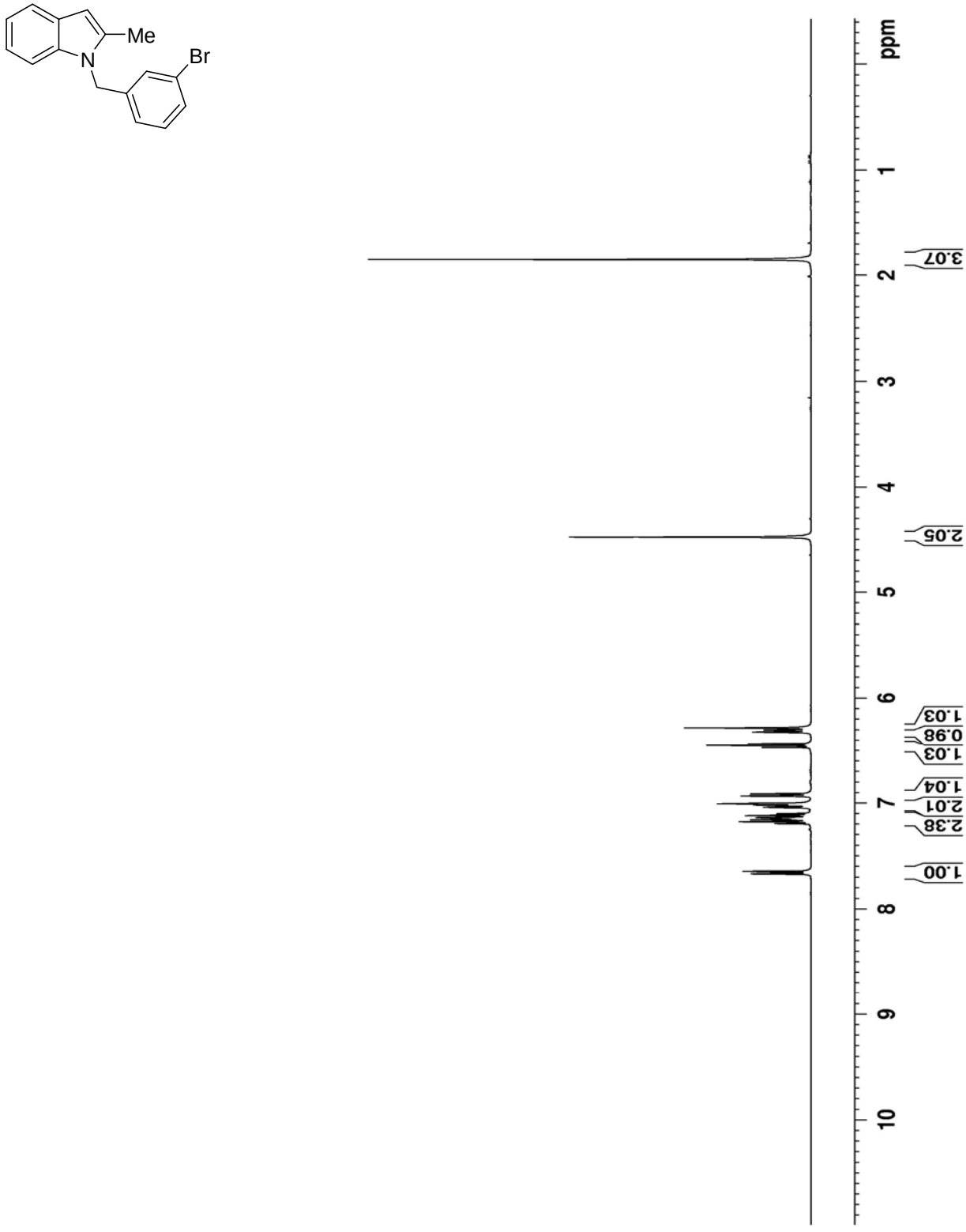




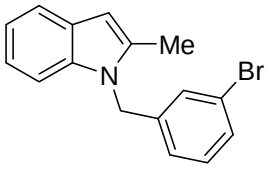
^{13}C NMR spectrum of B (100 MHz, $CDCl_3$)

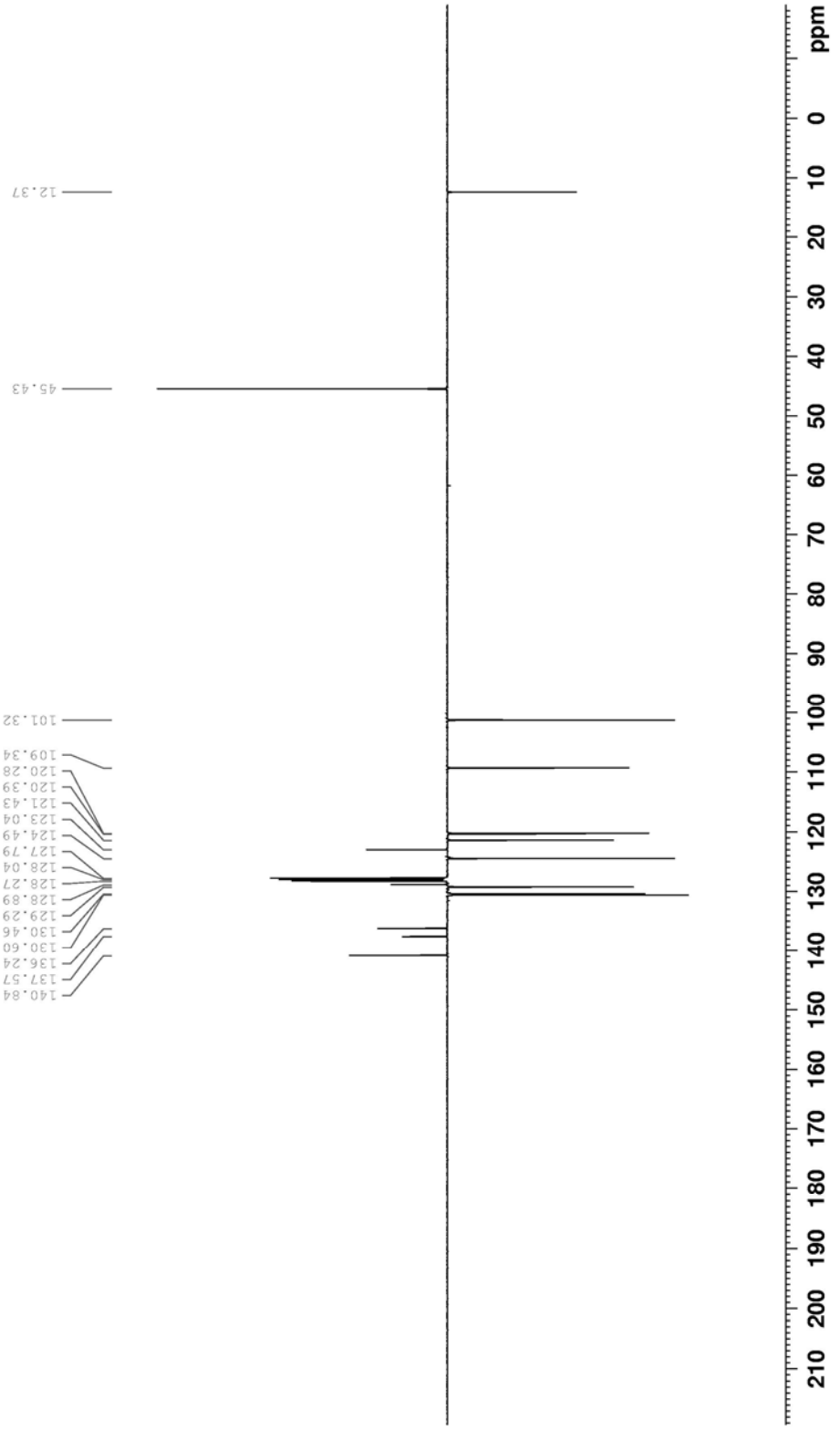


^{1}H NMR of C (400 MHz, C_6D_6)

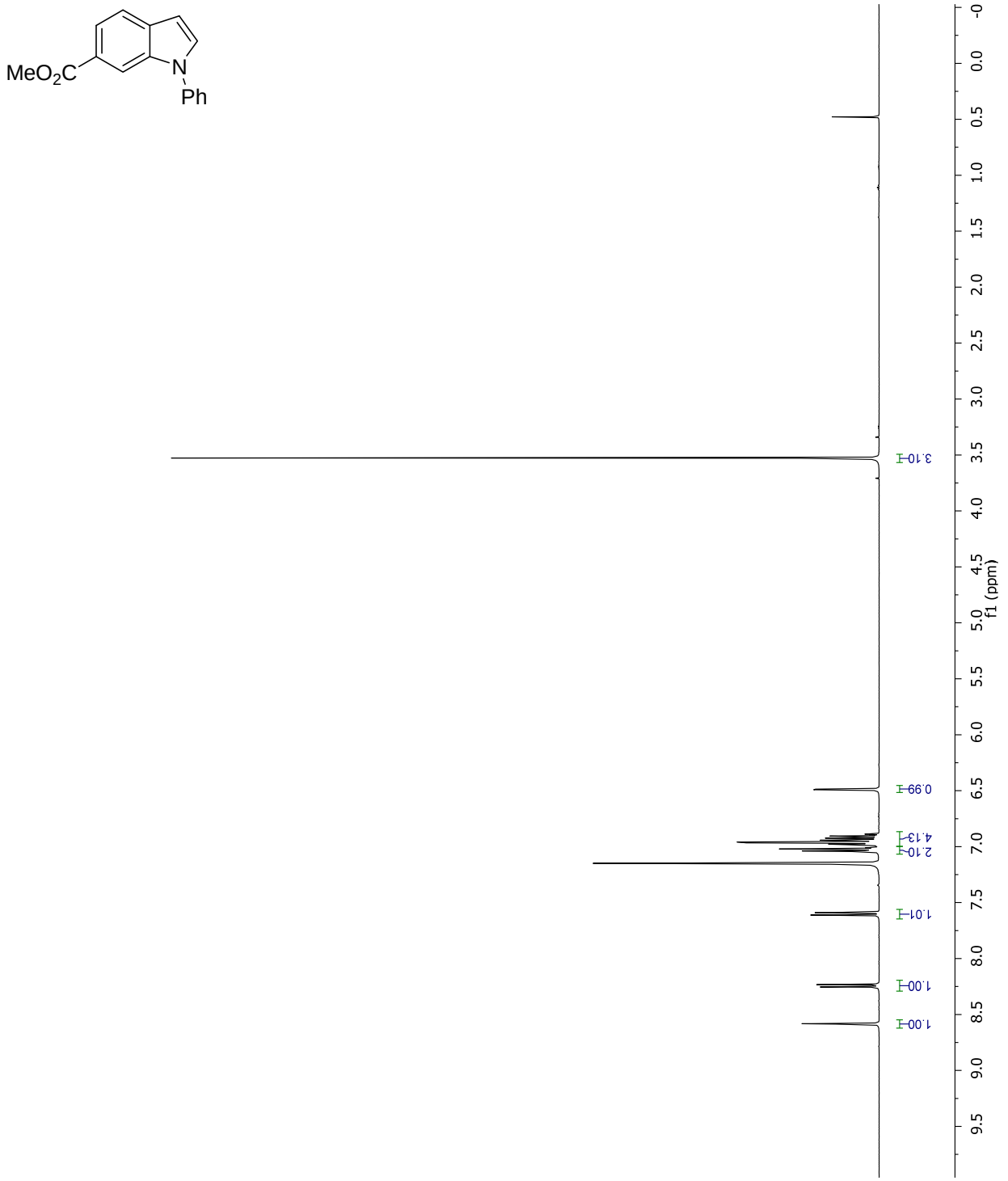


^{13}C NMR spectrum of C (100 MHz, C_6D_6)

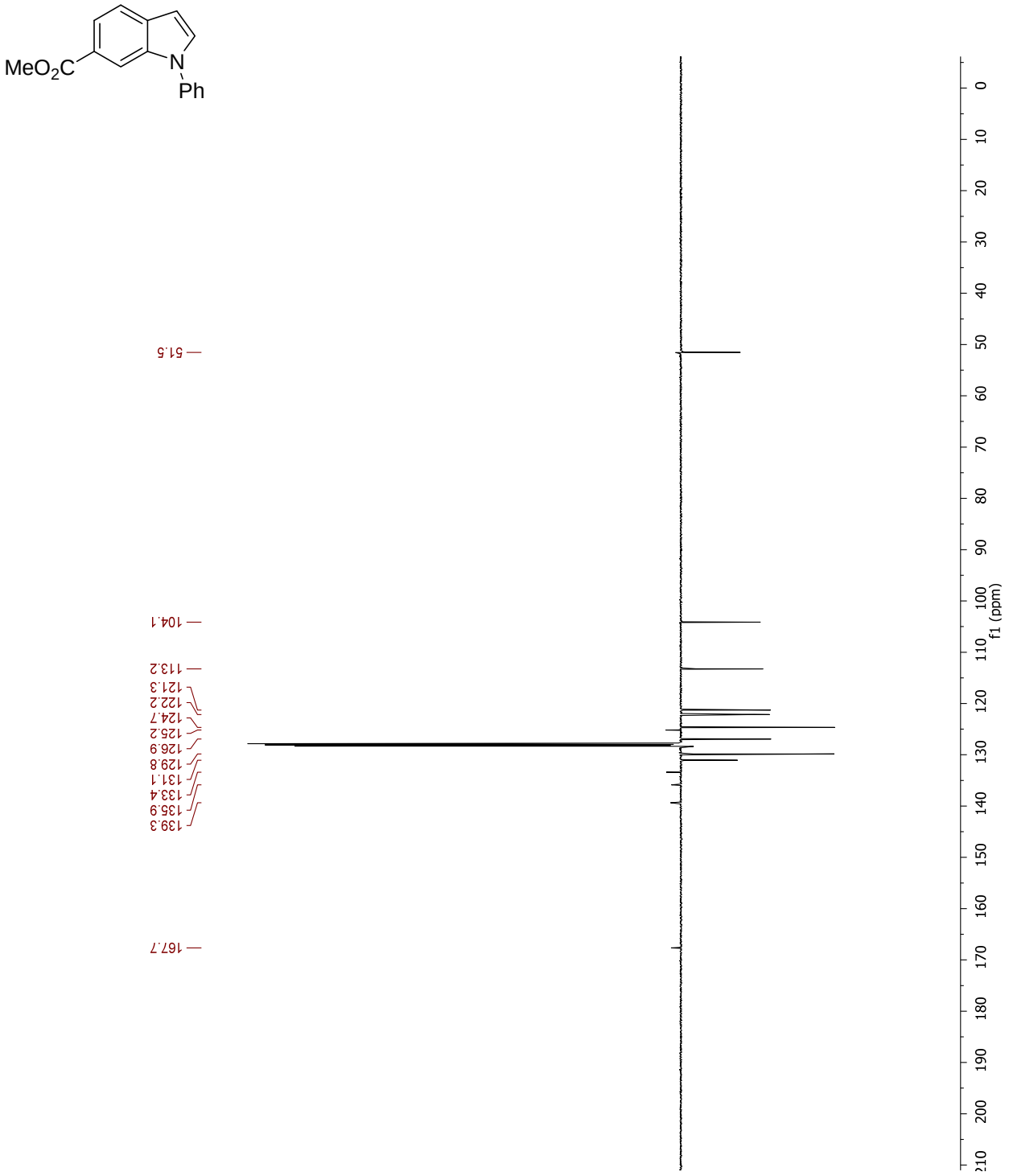




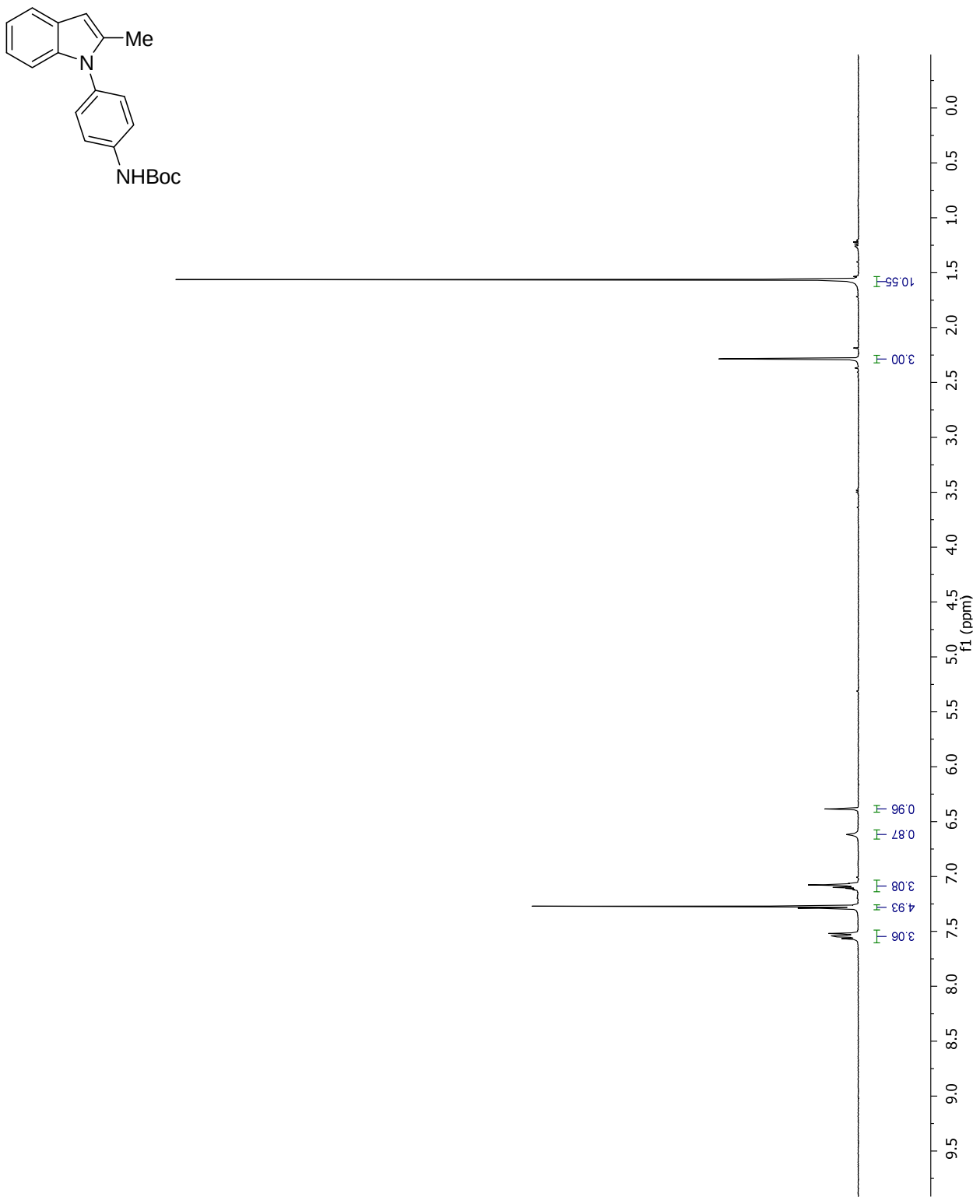
^{1}H NMR of D (400 MHz, C_6D_6)



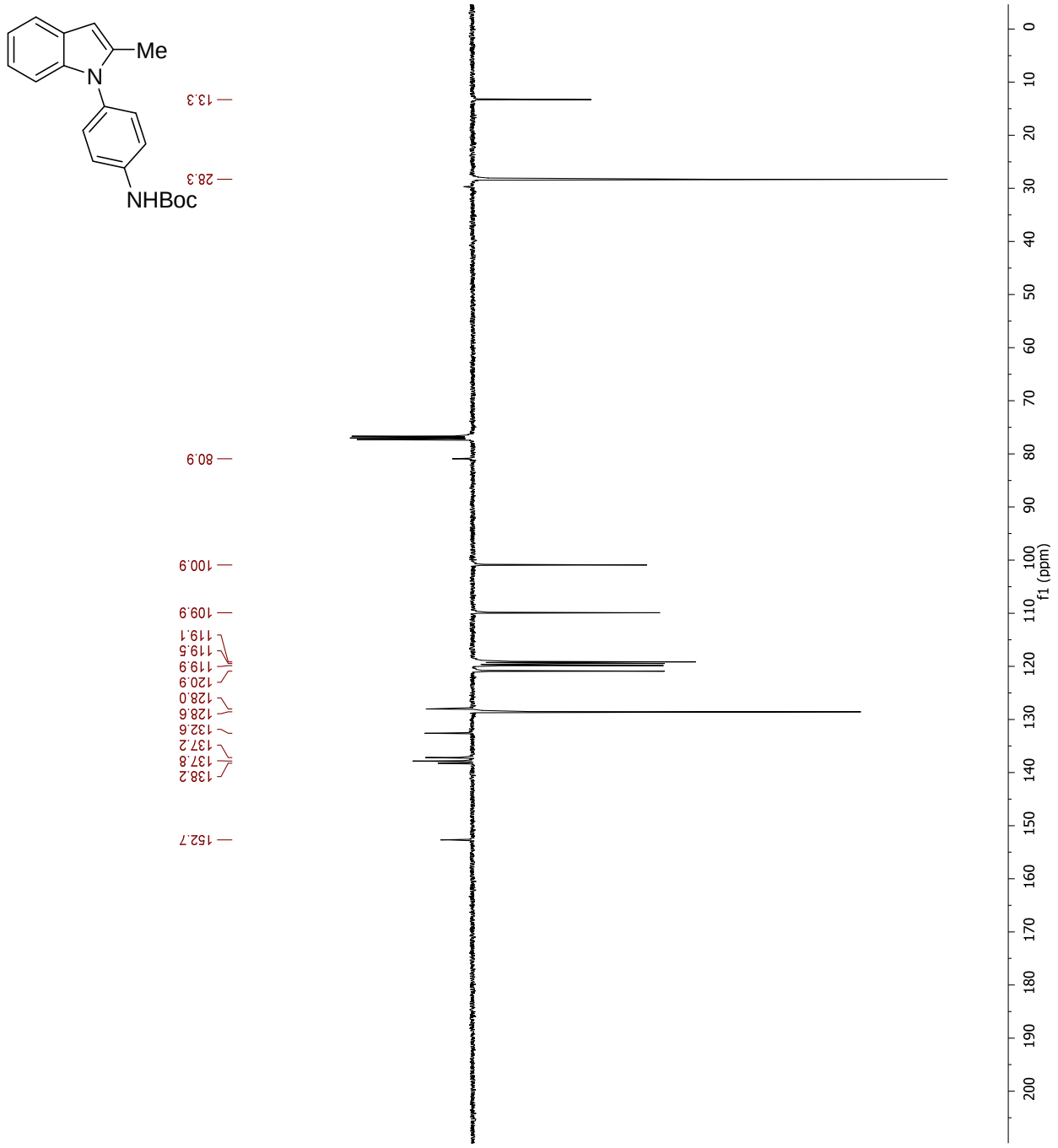
^{13}C NMR of D (400 MHz, C_6D_6)



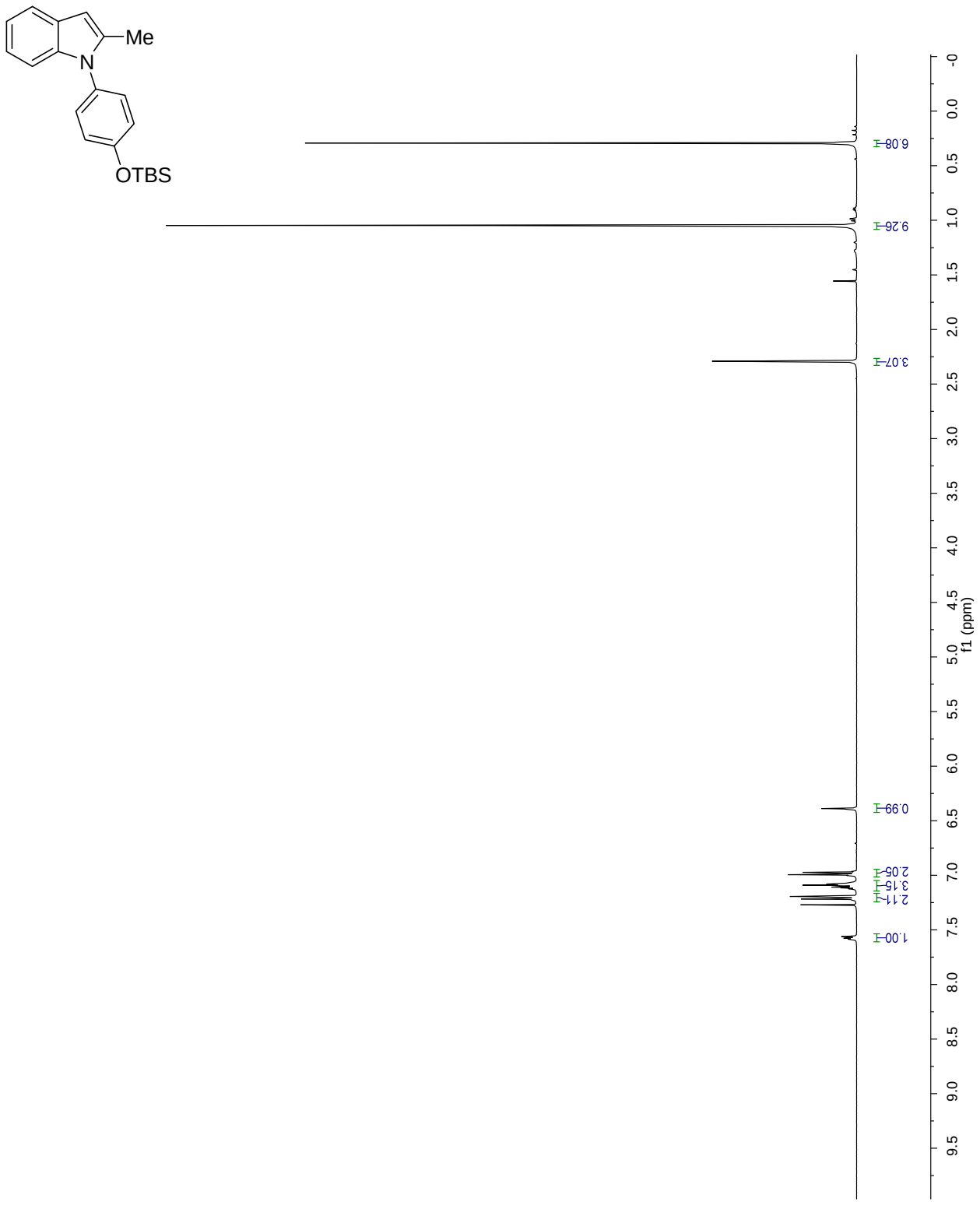
^{1}H NMR of E (400 MHz, $CDCl_3$)



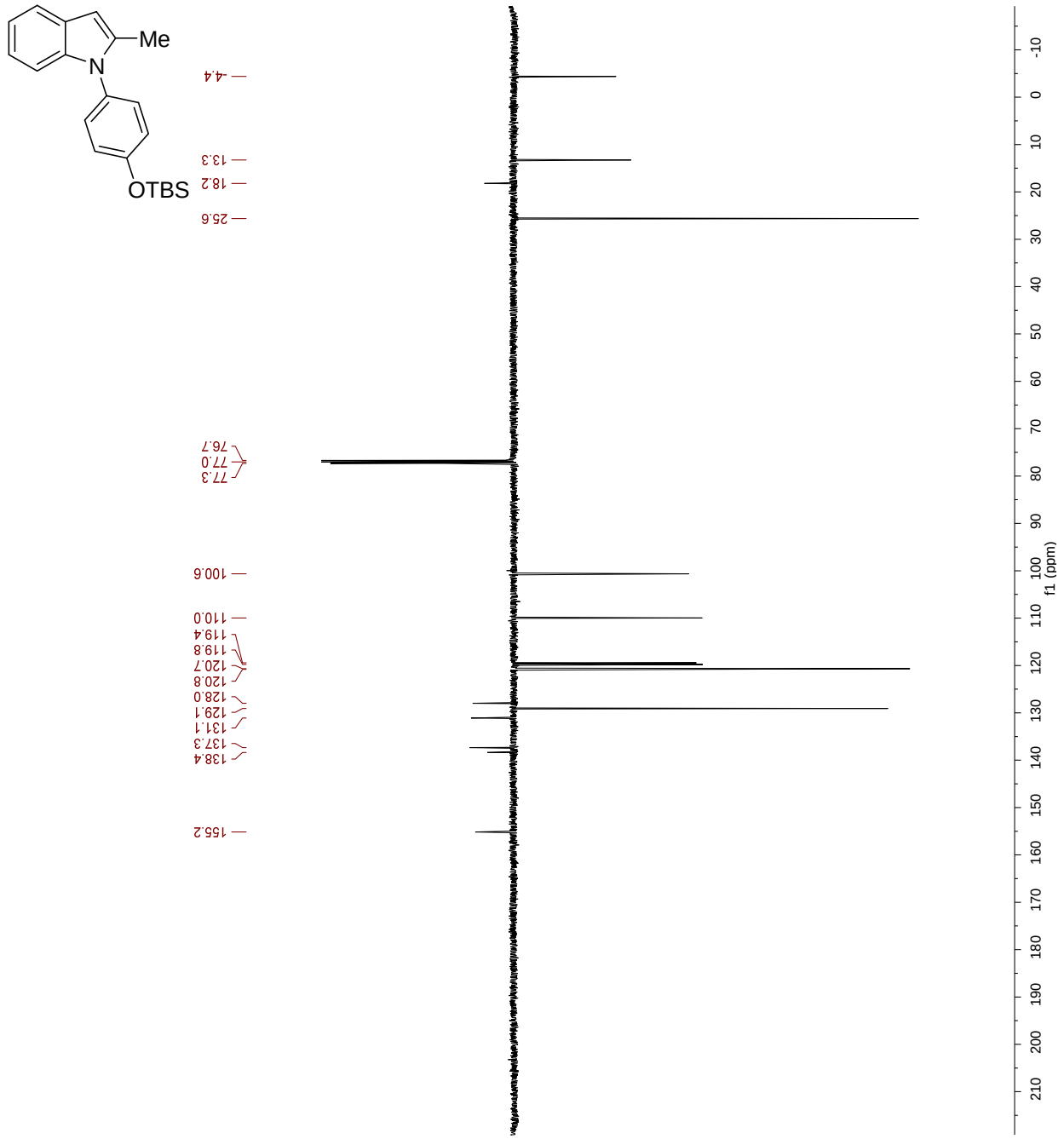
^{13}C NMR of E (400 MHz, $CDCl_3$)



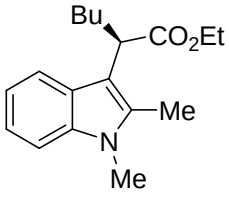
^{1}H NMR of F (400 MHz, $CDCl_3$)

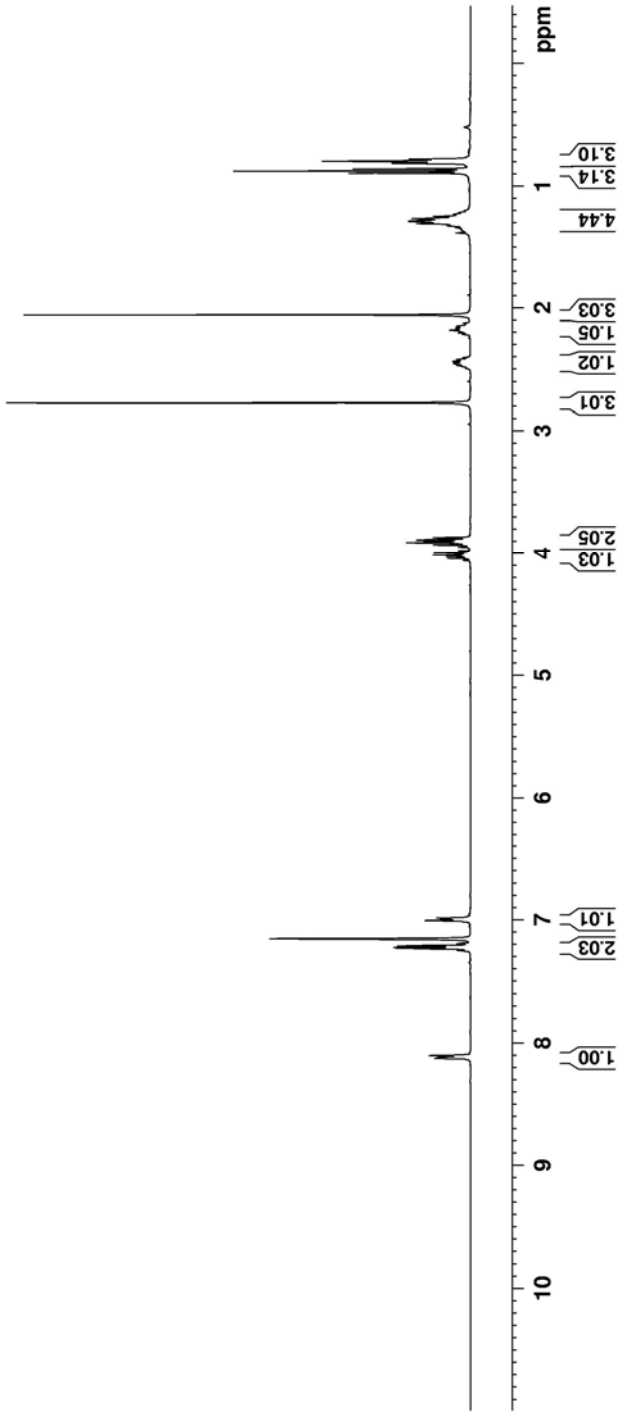


^{13}C NMR of F (400 MHz, $CDCl_3$)

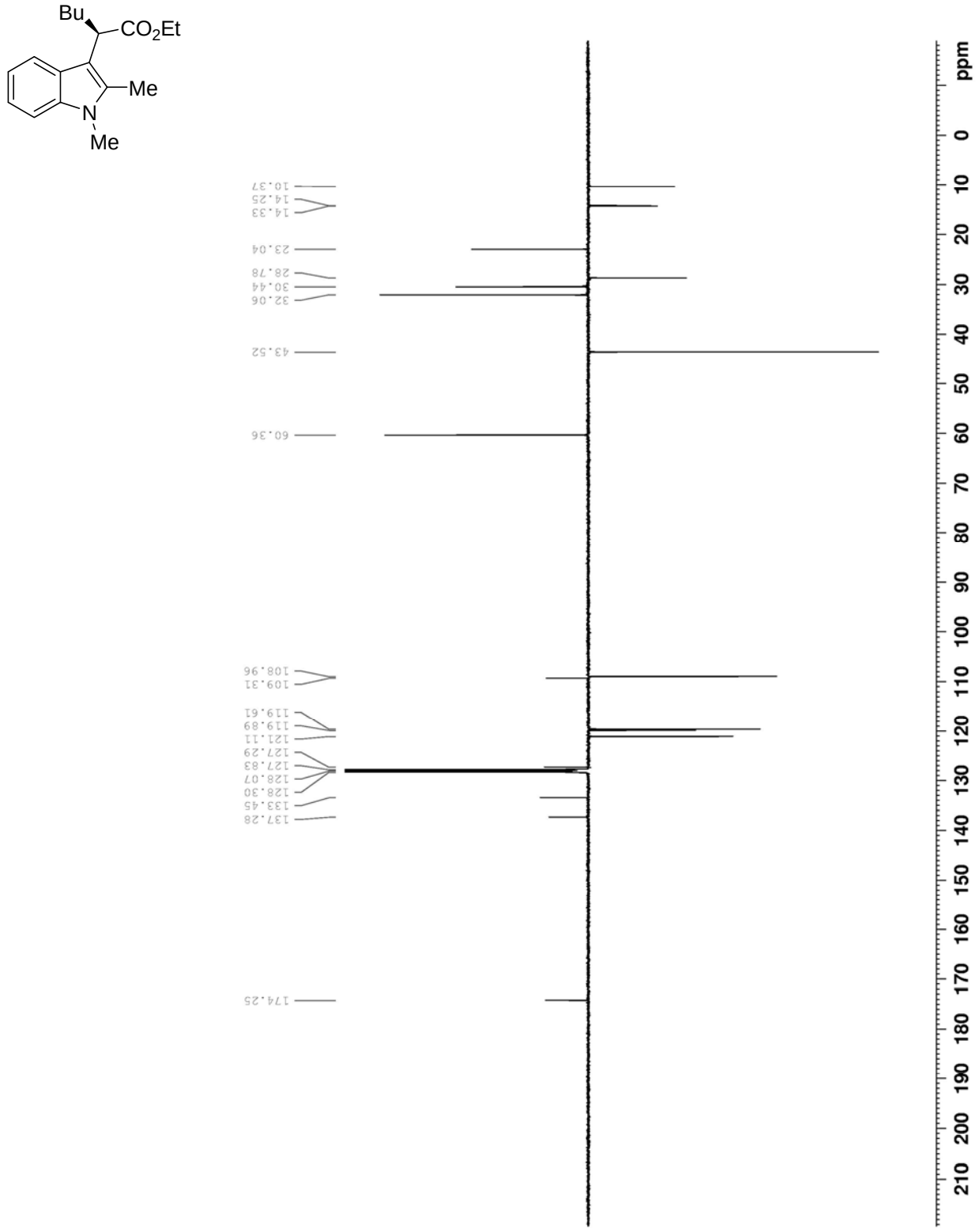


^{1}H NMR of 1 (400 MHz, C_6D_6)

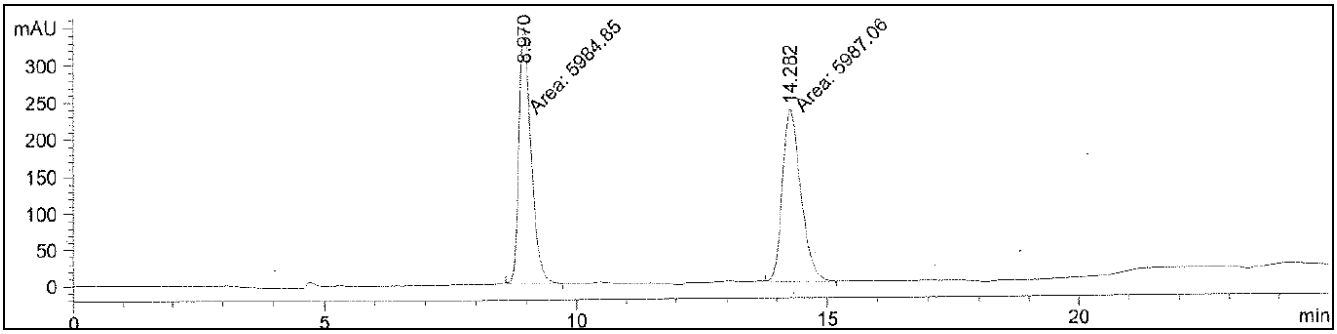




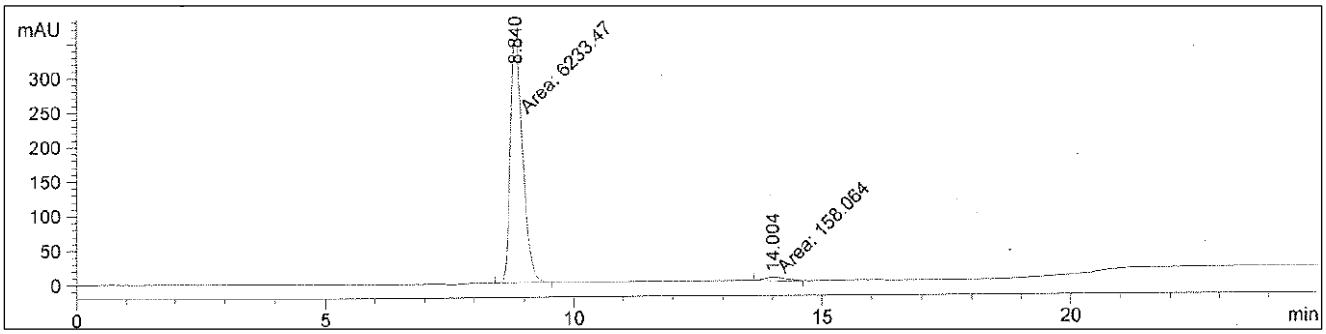
^{13}C NMR spectrum of 1 (100 MHz, C_6D_6)



HPLC resolution of racemic **1** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



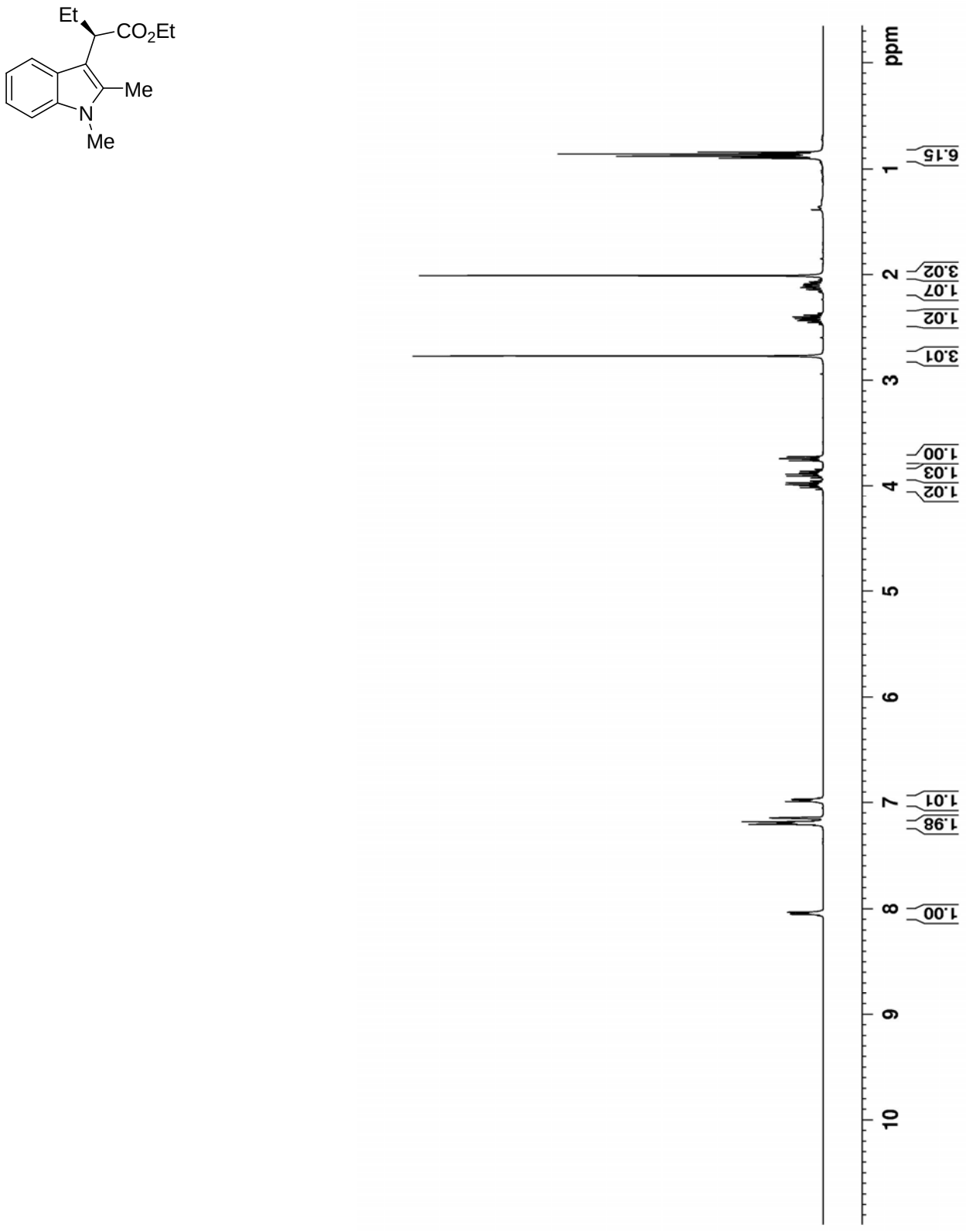
Enantiomeric excess of **1** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



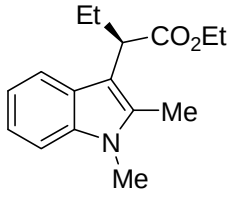
Signal 2: DAD1 B, Sig=220,4 Ref=450,80

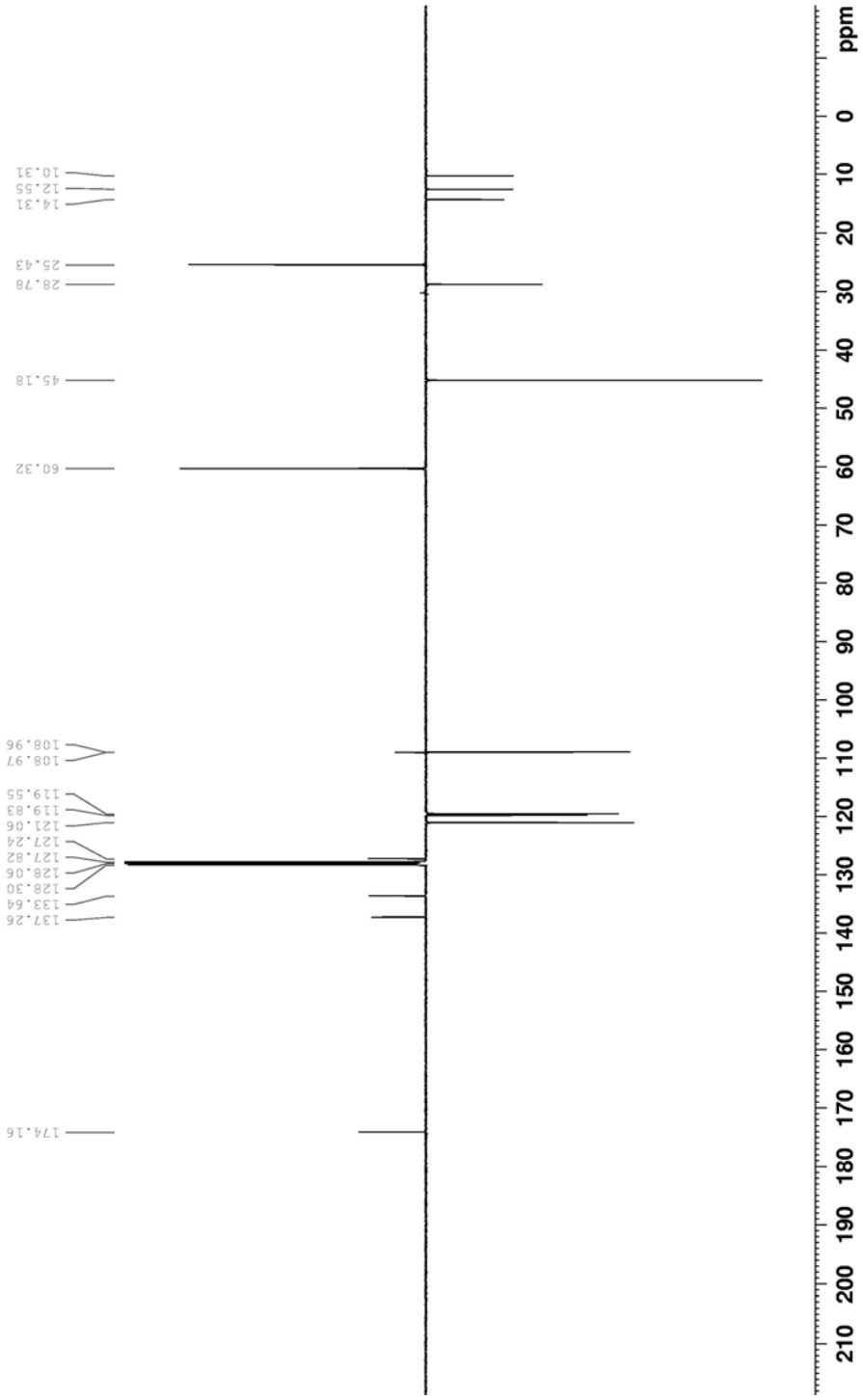
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.840	MM	0.2825	6233.46729	367.79446	97.5270
2	14.004	MM	0.5361	158.06422	4.91373	2.4730
Totals :				6391.53151	372.70820	

^{1}H NMR of 2 (400 MHz, C_6D_6)

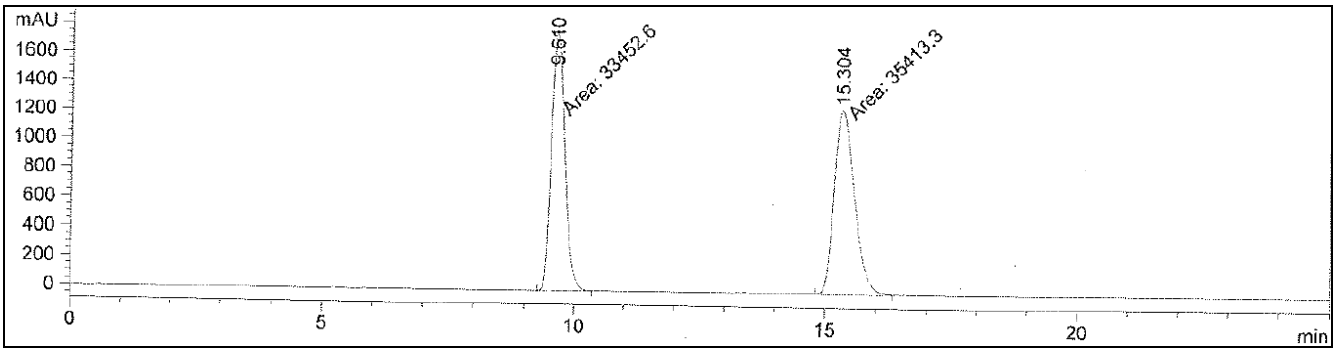


^{13}C NMR spectrum of 2 (100 MHz, C_6D_6)

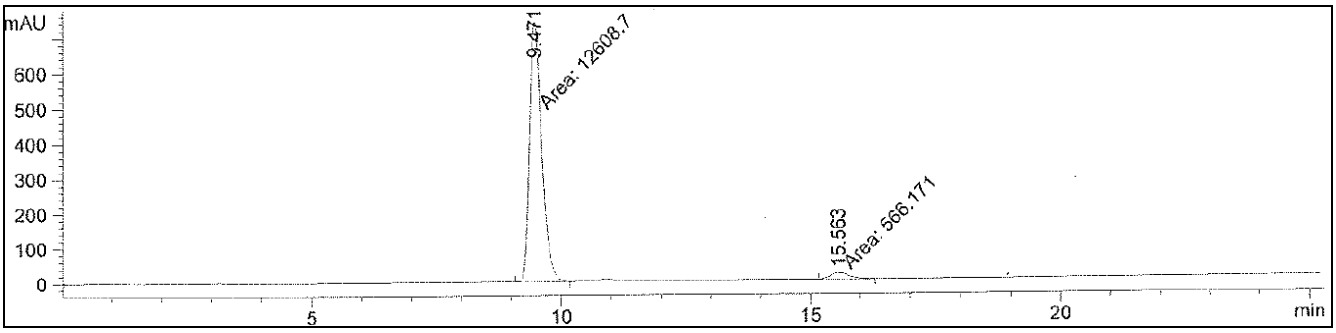




HPLC resolution of racemic **2** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



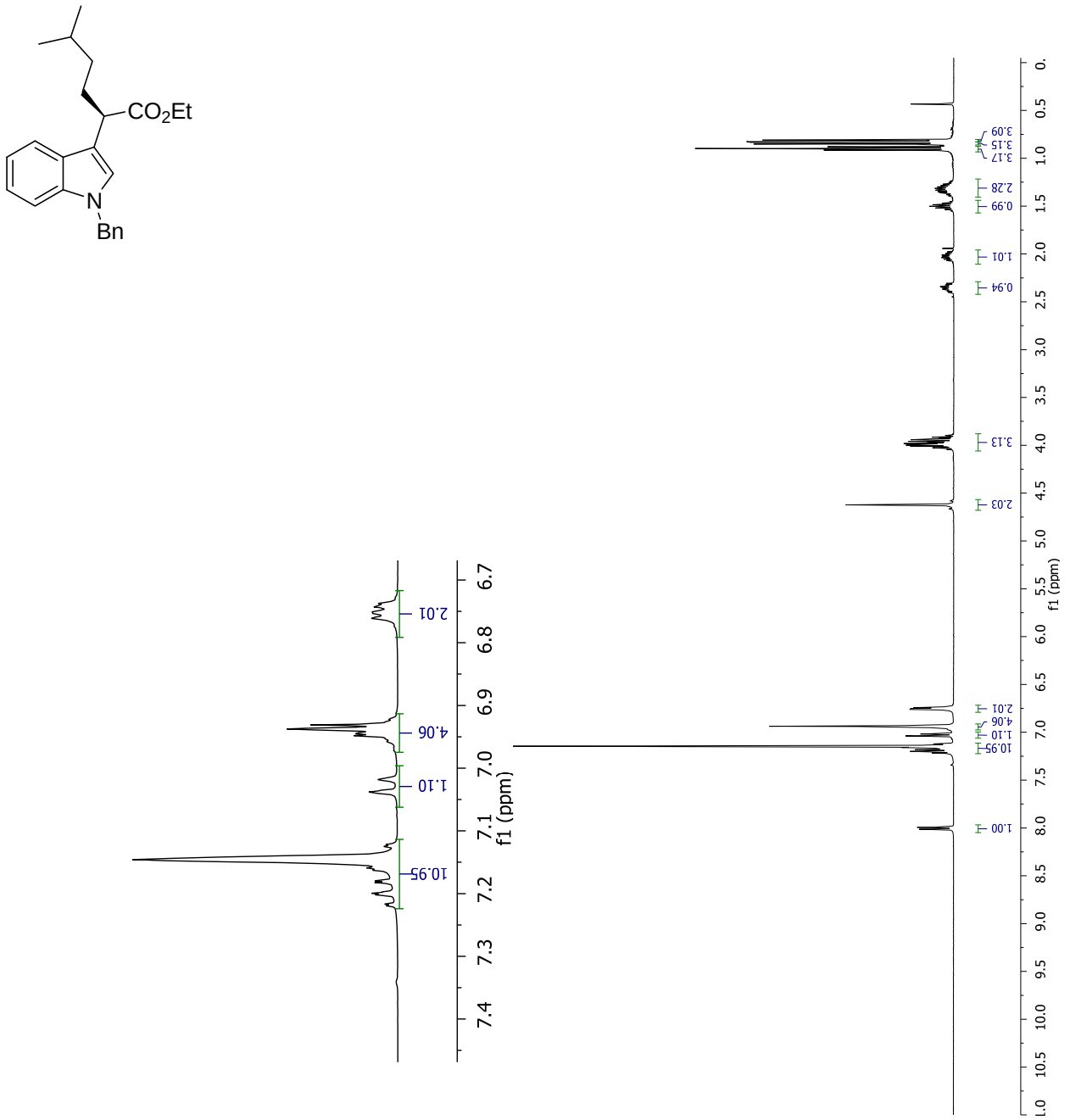
Enantiomeric excess of **2** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



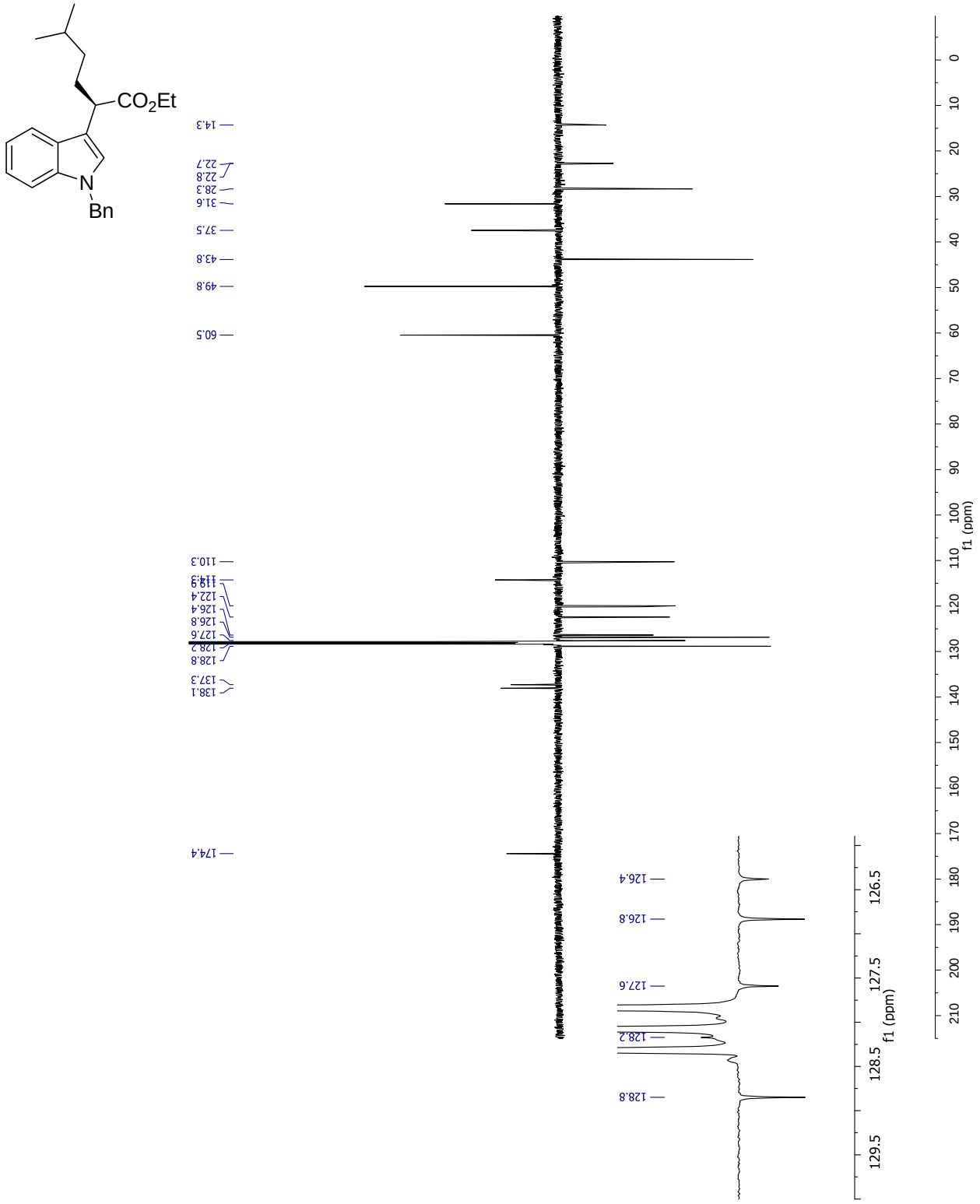
Signal 2: DAD1 B, Sig=220,4 Ref=450,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.471	MM	0.2835	1.26087e4	741.28253	95.7026
2	15.563	MM	0.4738	566.17084	19.91690	4.2974
Totals :				1.31749e4	761.19943	

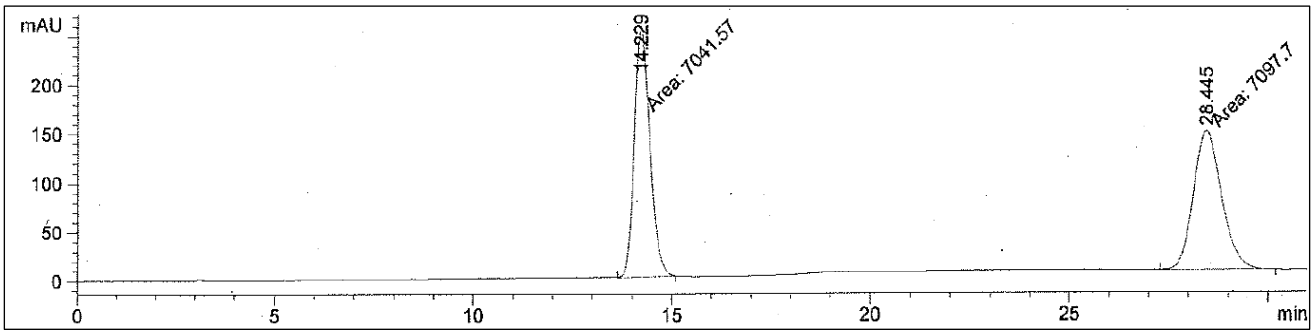
^{1}H NMR Spectrum of **3** (400 MHz, C_6D_6)



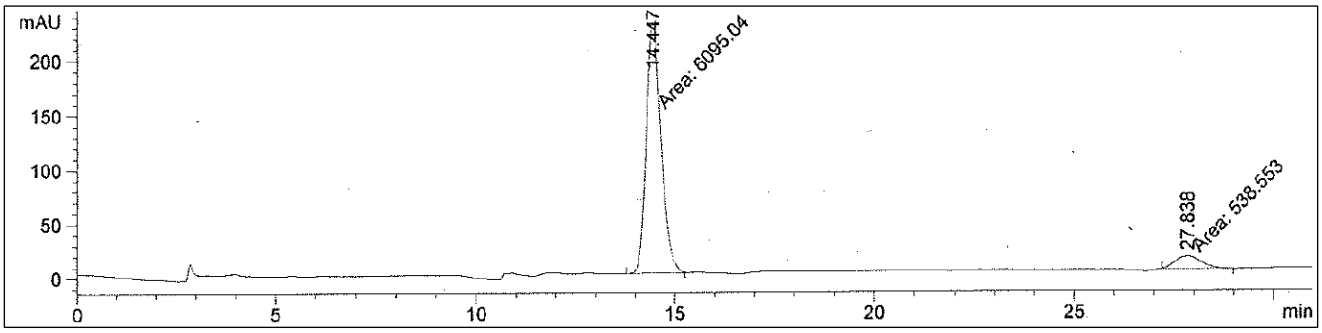
^{13}C NMR Spectrum of **3** (100 MHz, C_6D_6)



HPLC resolution of racemic **3** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)

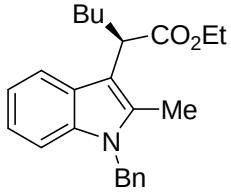


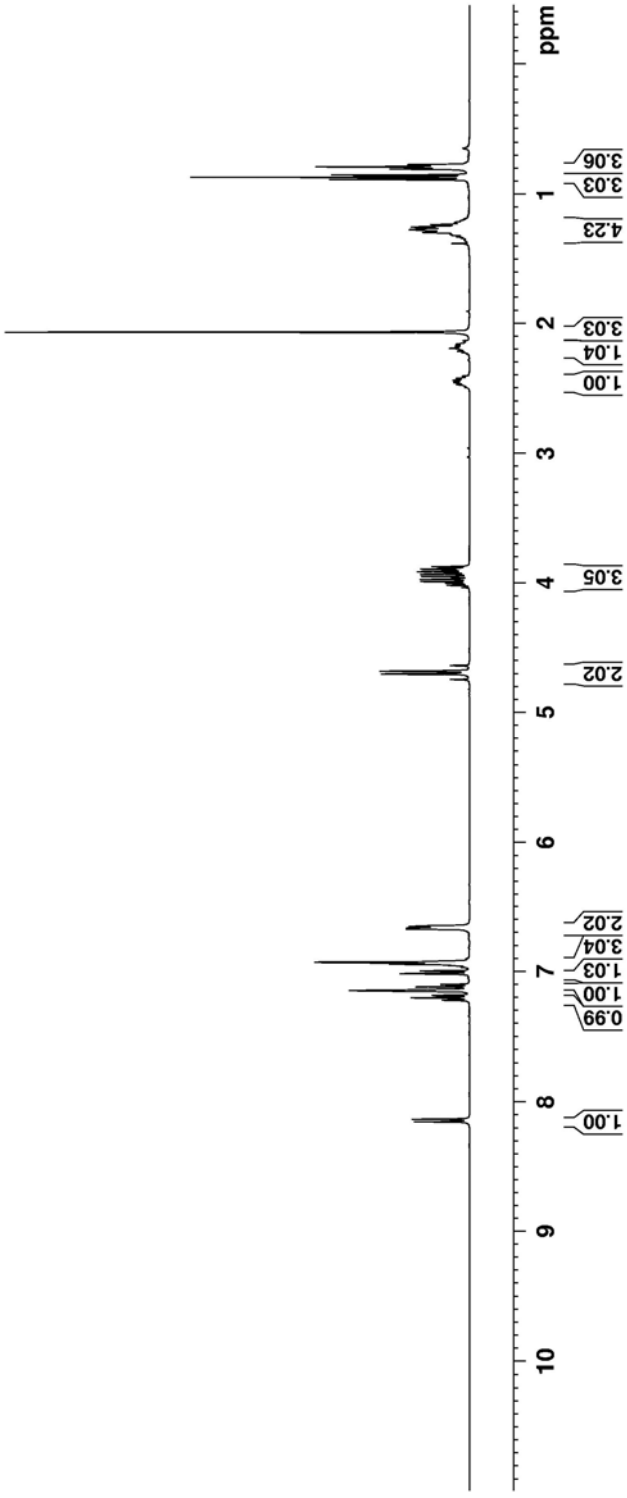
Enantiomeric excess of **3** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



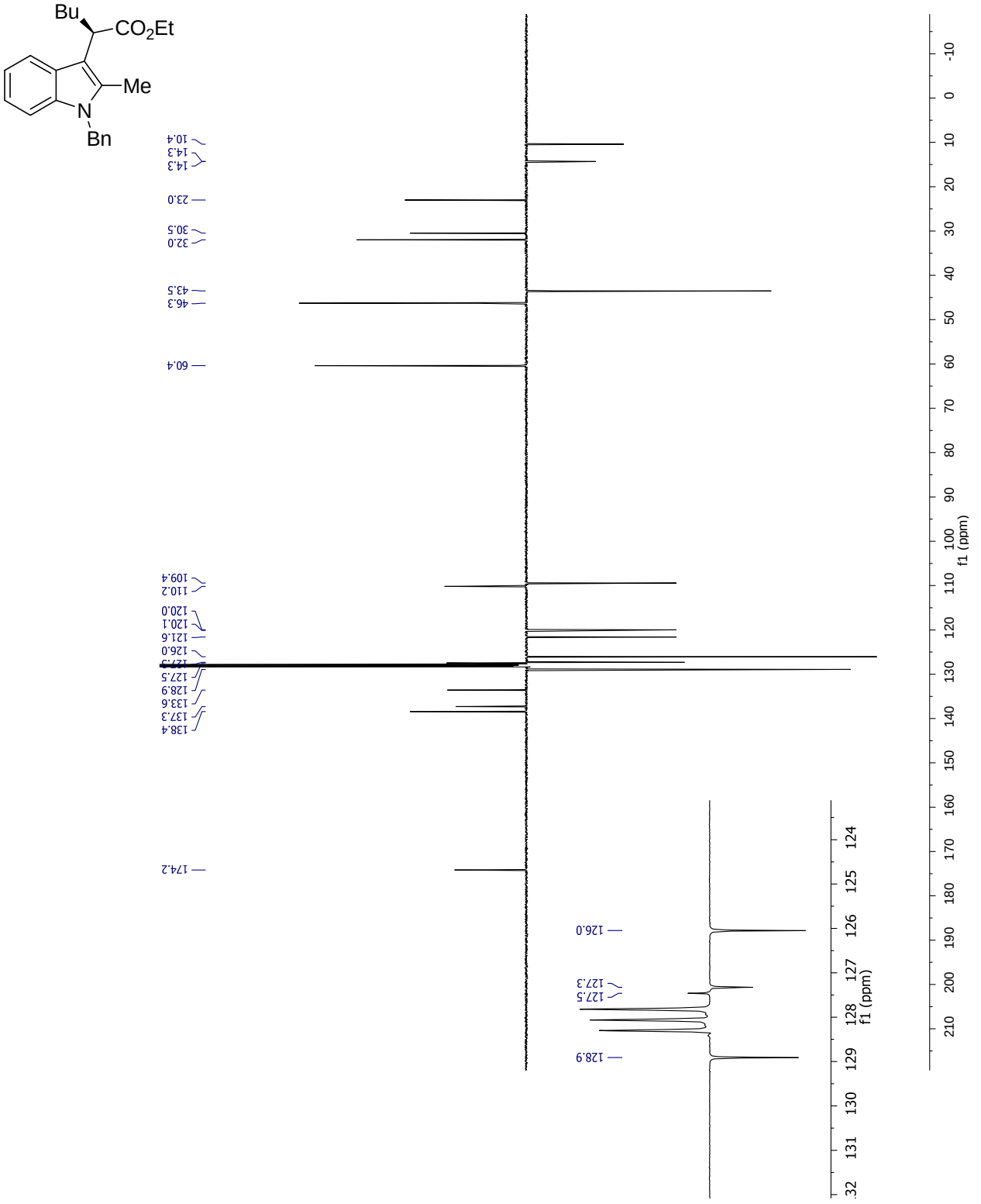
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.447	MM	0.4411	6095.04443	230.31833	91.8814
2	27.838	MM	0.7484	538.55341	11.99318	8.1186
Totals :				6633.59784	242.31151	

^{1}H NMR of 4 (400 MHz, C_6D_6)

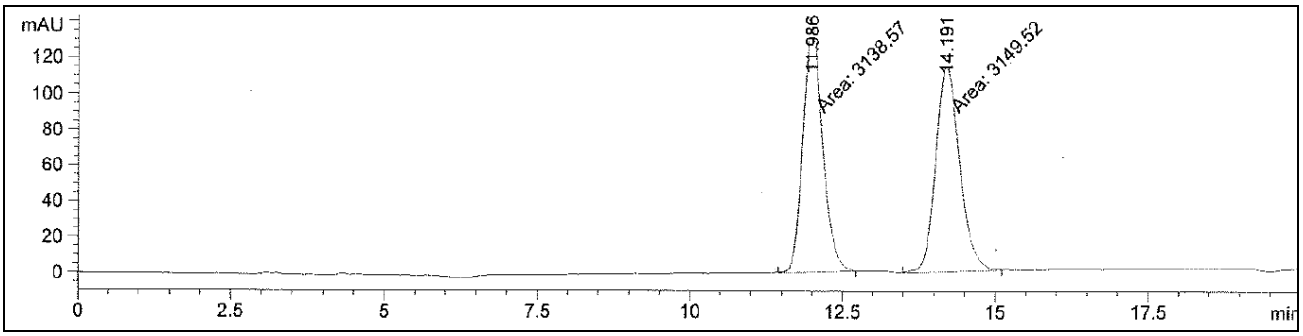




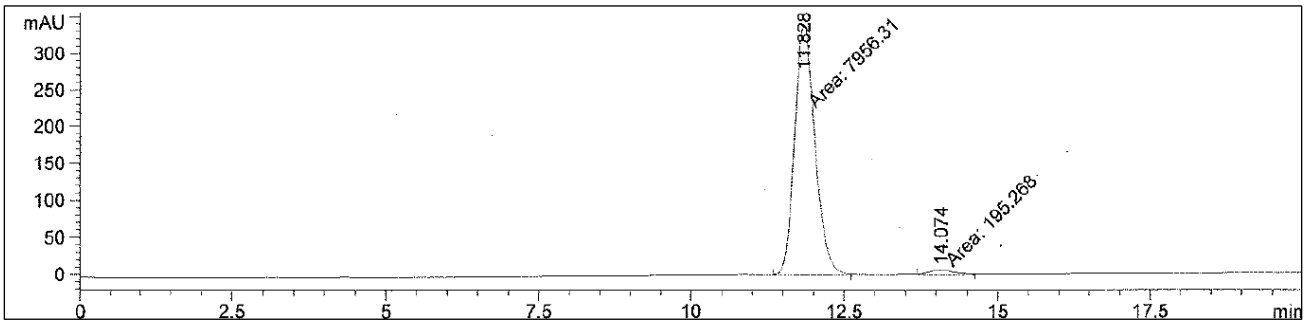
^{13}C NMR spectrum of 4 (100 MHz, C_6D_6)



HPLC resolution of racemic **4** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



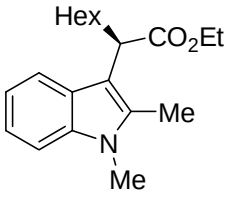
Enantiomeric excess of **4** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)

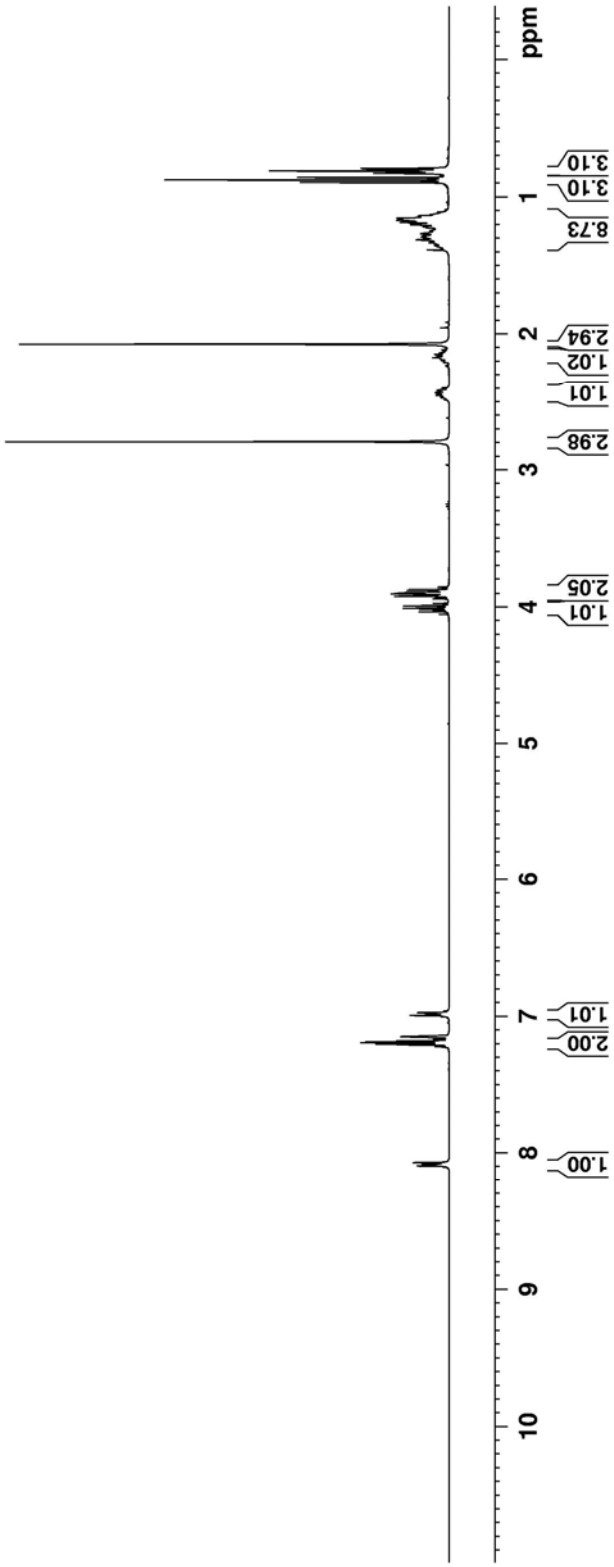


Signal 2: DAD1 B, Sig=220,4 Ref=450,80

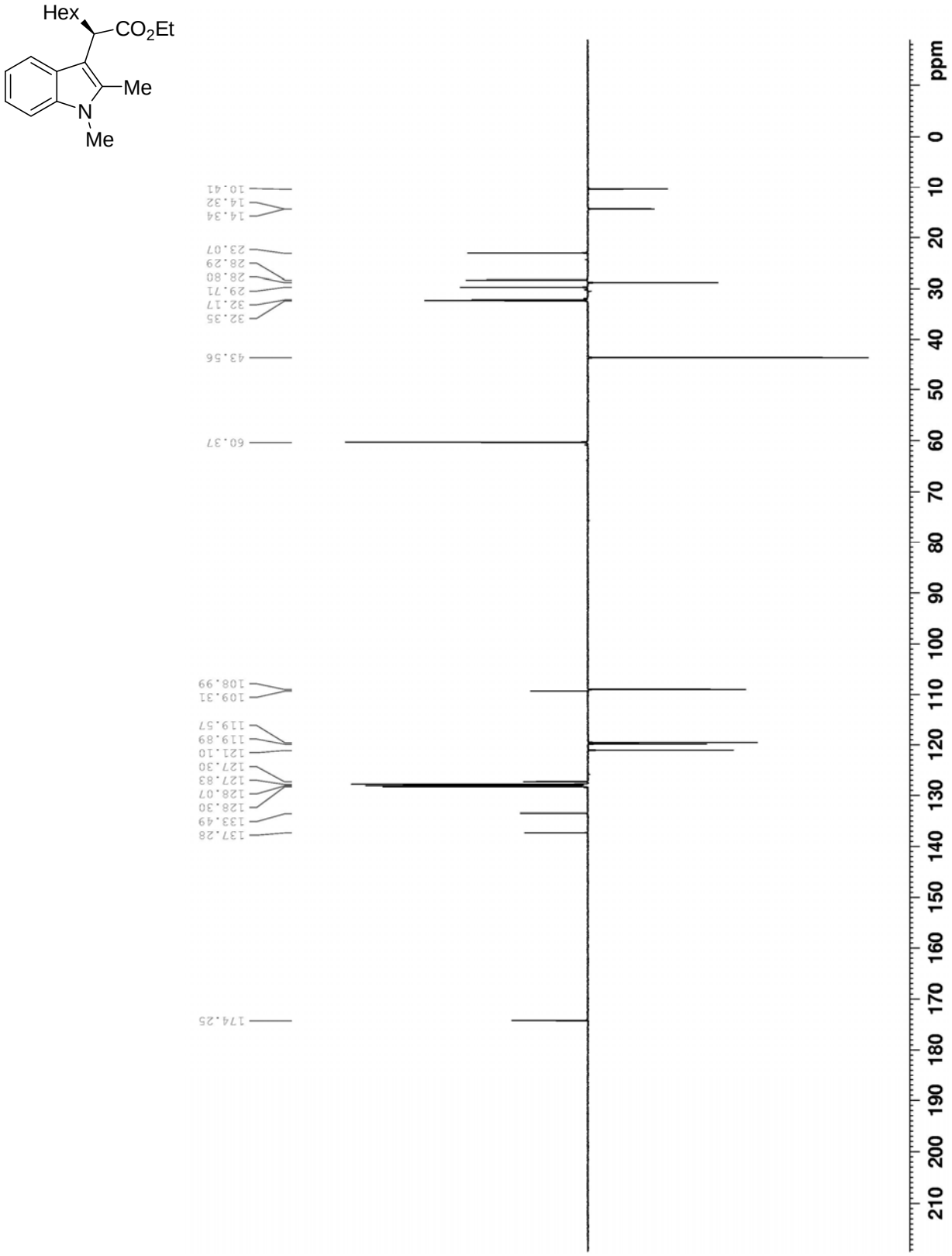
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.828	MM	0.3896	7956.31396	340.40134	97.6045
2	14.074	MM	0.4958	195.26753	6.56409	2.3955
Totals :				8151.58150	346.96543	

^{1}H NMR of 5 (400 MHz, C_6D_6)

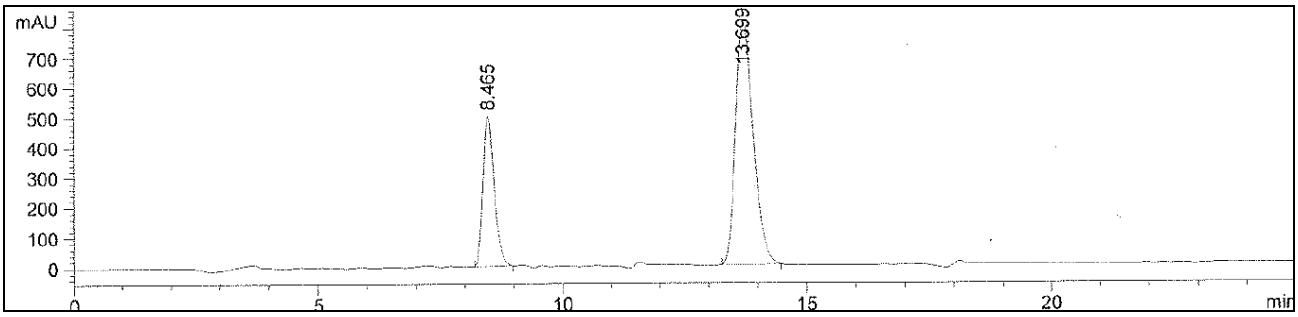




^{13}C NMR spectrum of 5 (100 MHz, C_6D_6)

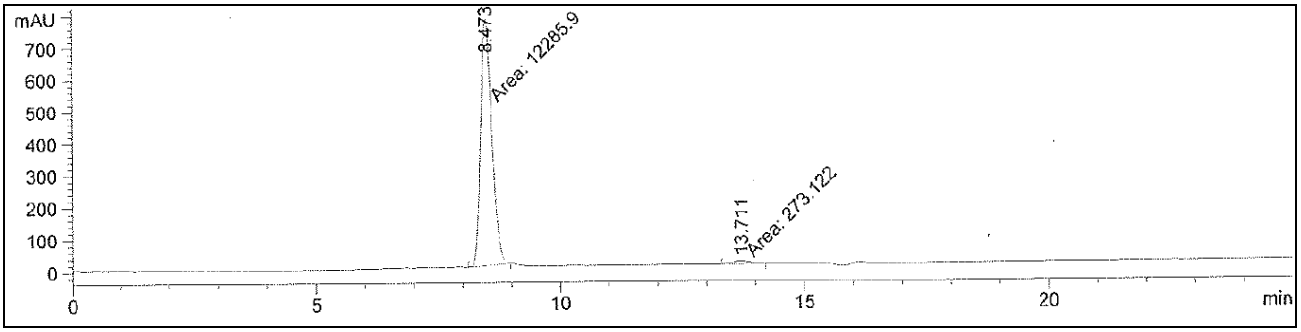


HPLC resolution of racemic **5** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



NOTE: "Racemic" material was prepared using a mechanical mixture of Rh_2(*S*-PTTL)$_4$ and Rh_2(*R*-PTTL)$_4$ which accounts for the inequivalent integration of the racemate.

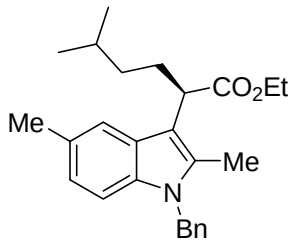
Enantiomeric excess of **5** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)

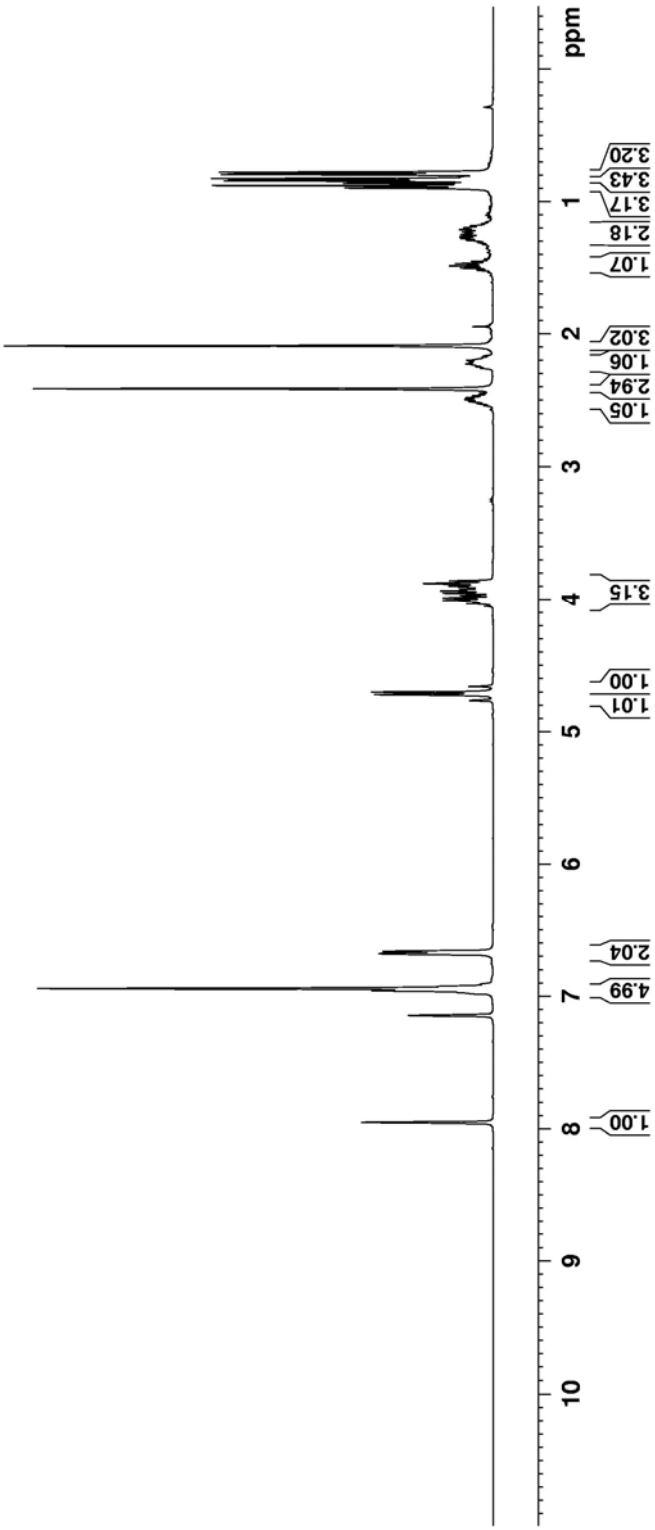


Signal 2: DAD1 B, Sig=220,4 Ref=450,80

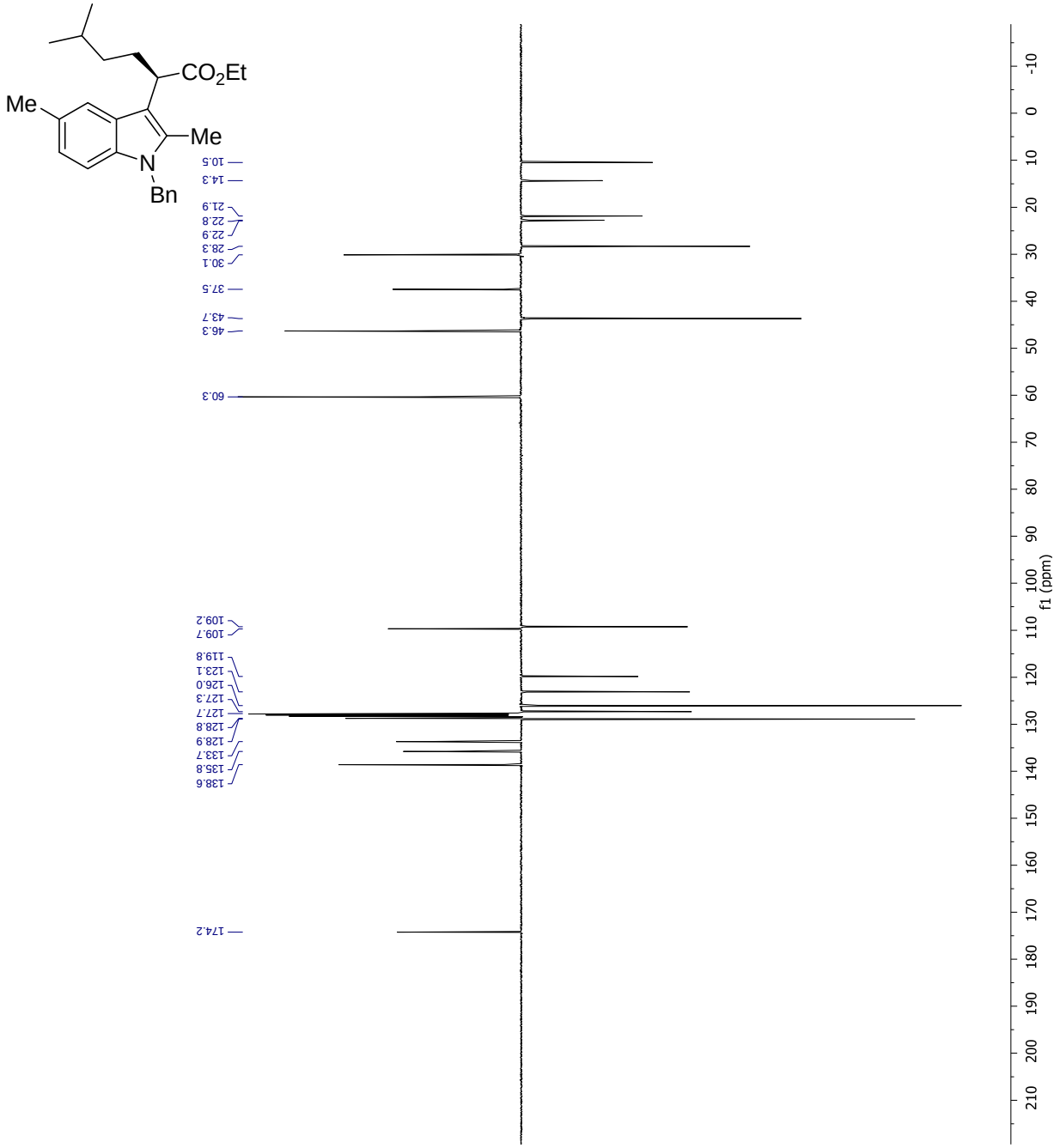
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.473	MM	0.2654	1.22859e4	771.41687	97.8253
2	13.711	MM	0.4223	273.12241	10.77975	2.1747
Totals :				1.25591e4	782.19662	

^{1}H NMR of 6 (400 MHz, C_6D_6)

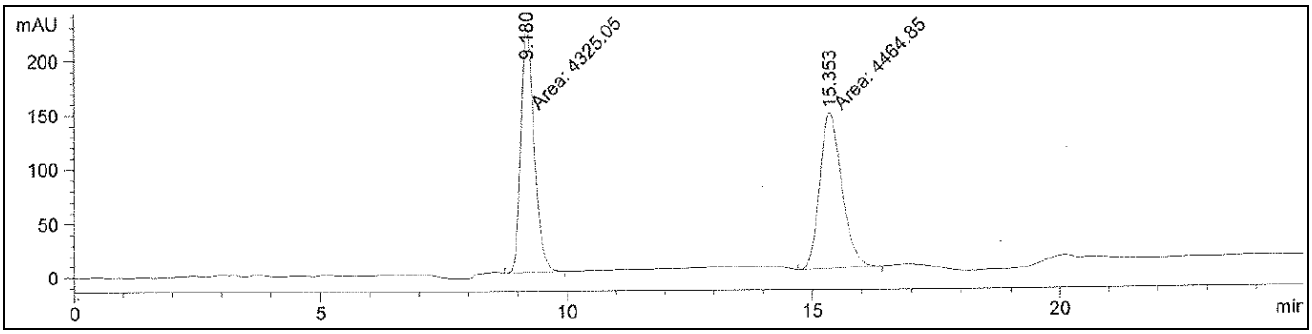




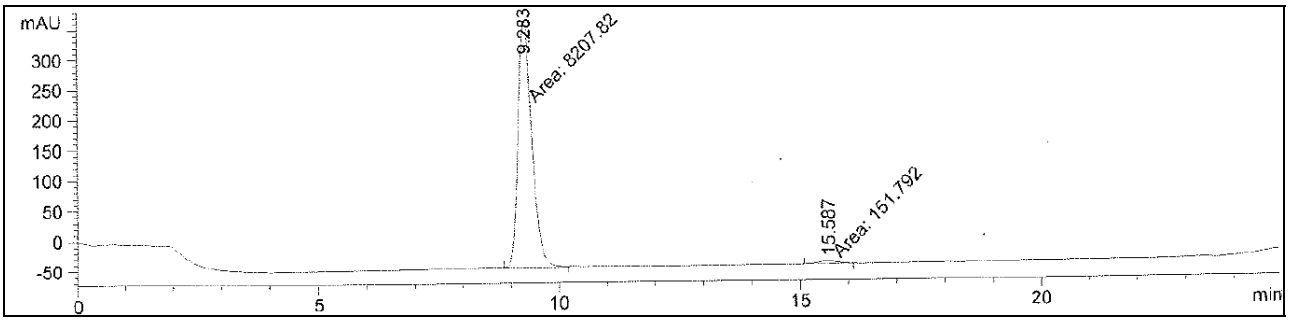
^{13}C NMR spectrum of 6 (100 MHz, C_6D_6)



HPLC resolution of racemic **6** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



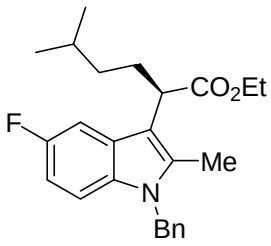
Enantiomeric excess of **6** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)

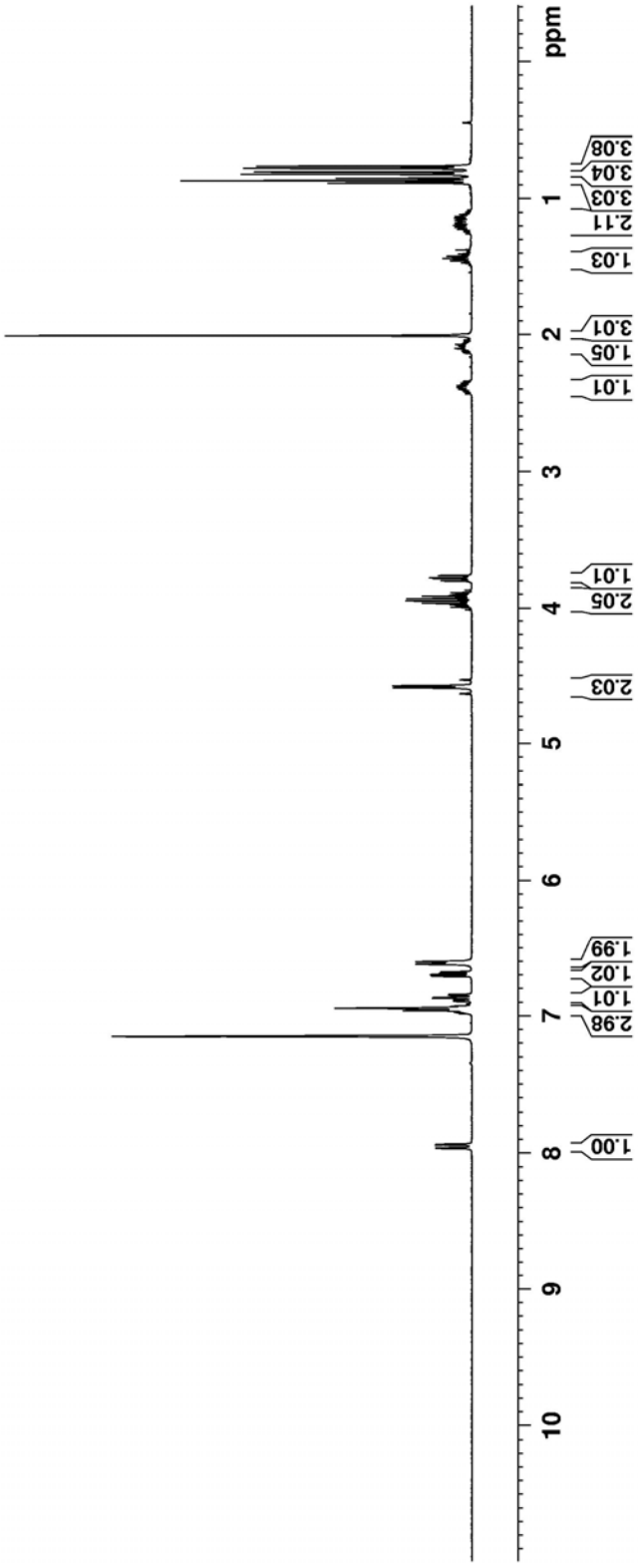


Signal 2: DAD1 B, Sig=220,4 Ref=450,80

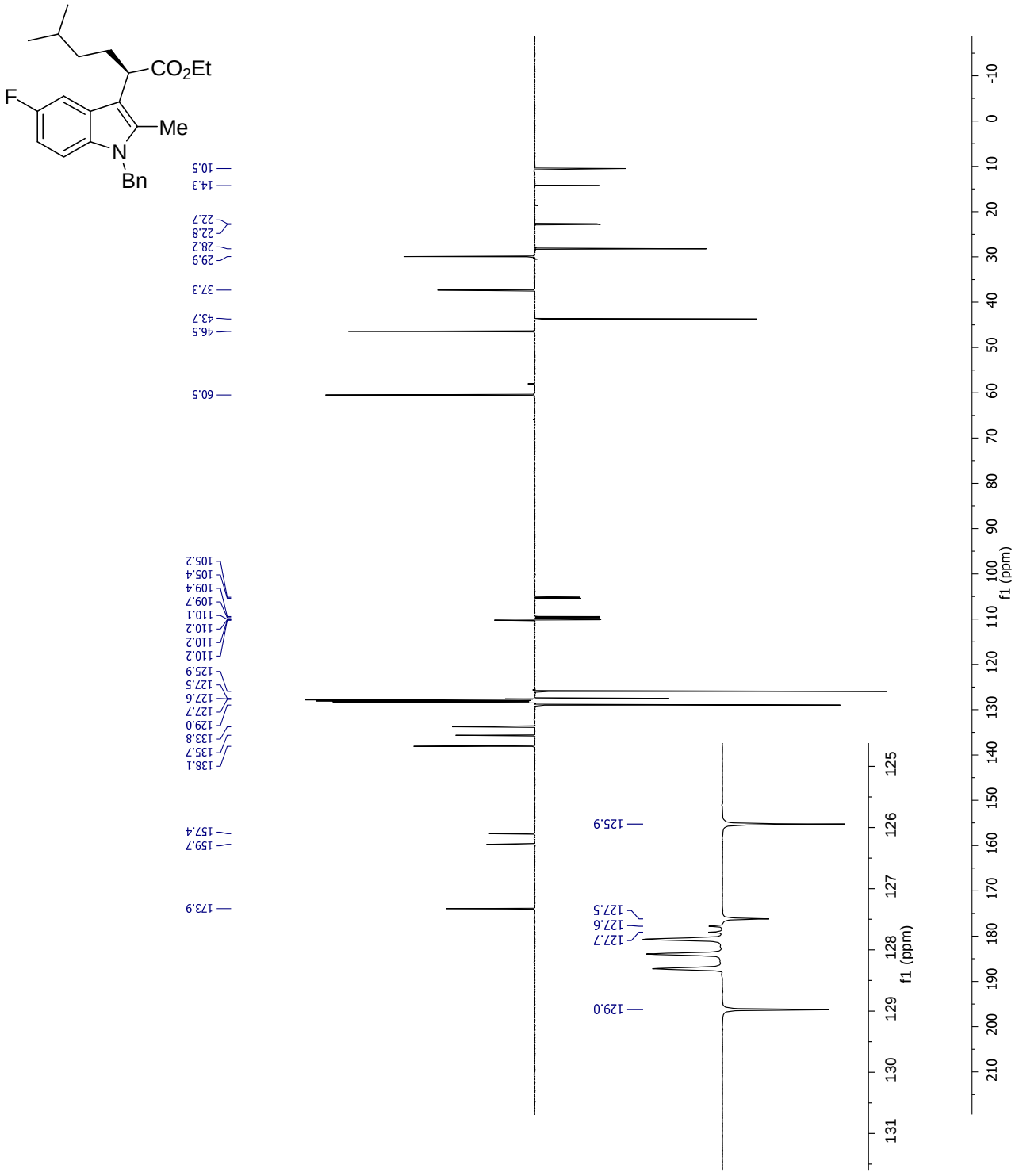
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.283	MM	0.3335	8207.82324	410.12985	98.1842
2	15.587	MM	0.5357	151.79230	4.72264	1.8158
Totals :				8359.61554	414.85249	

^{1}H NMR of 7 (400 MHz, C_6D_6)

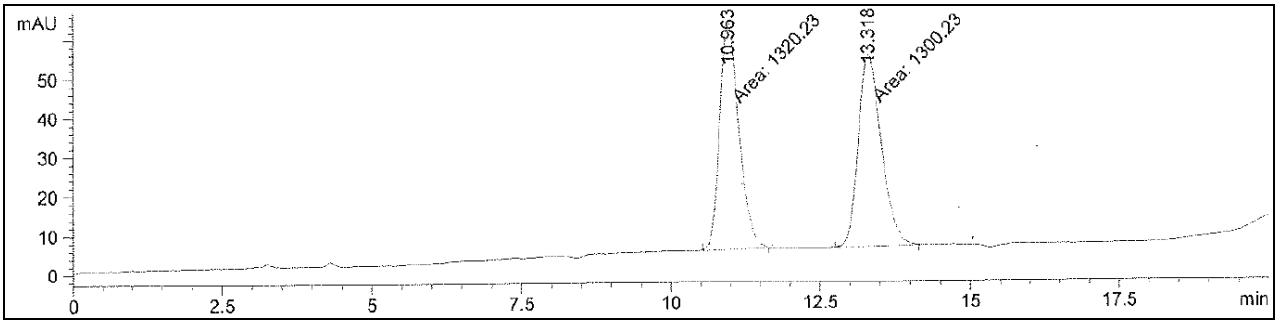




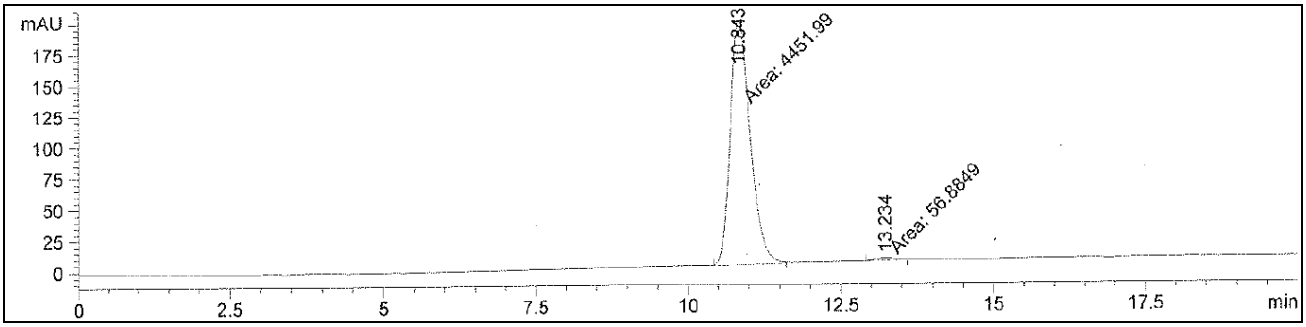
^{13}C NMR spectrum of 7 (100 MHz, C_6D_6)



HPLC resolution of racemic **7** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



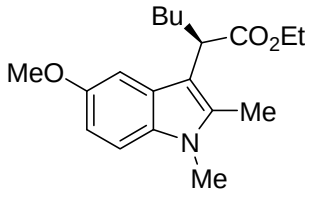
Enantiomeric excess of **7** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)

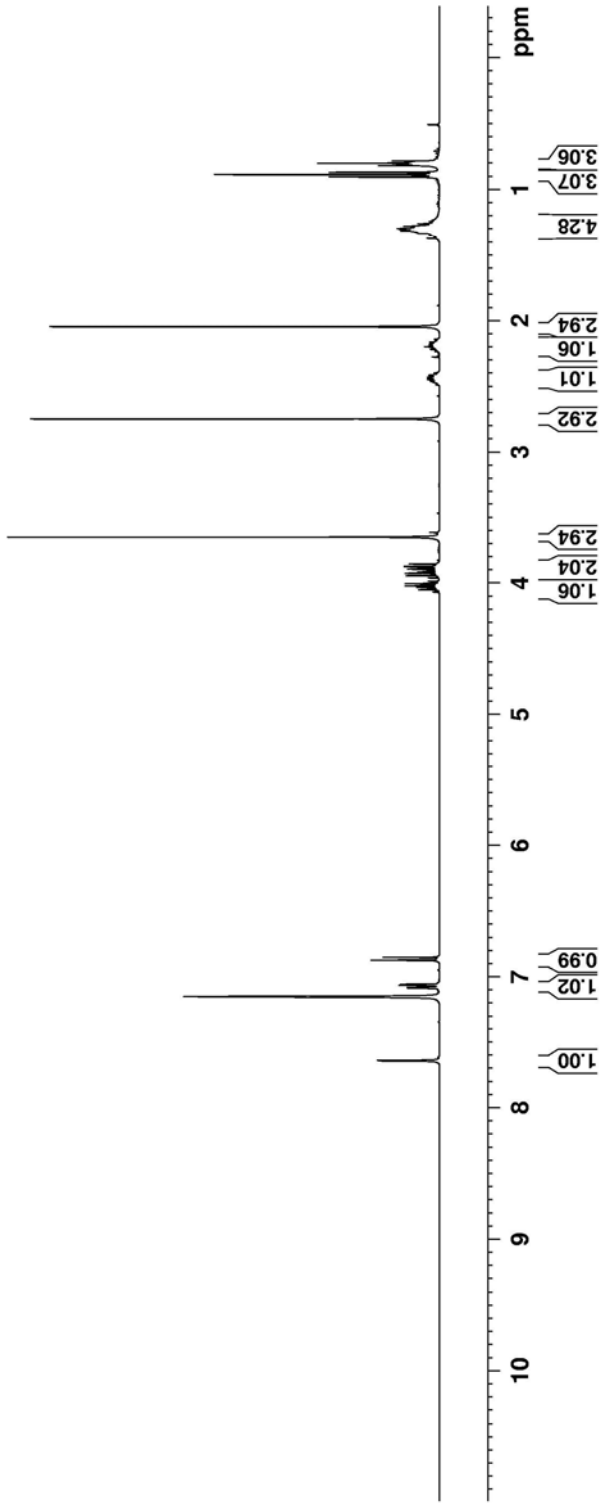


Signal 2: DAD1 B, Sig=220,4 Ref=450,80

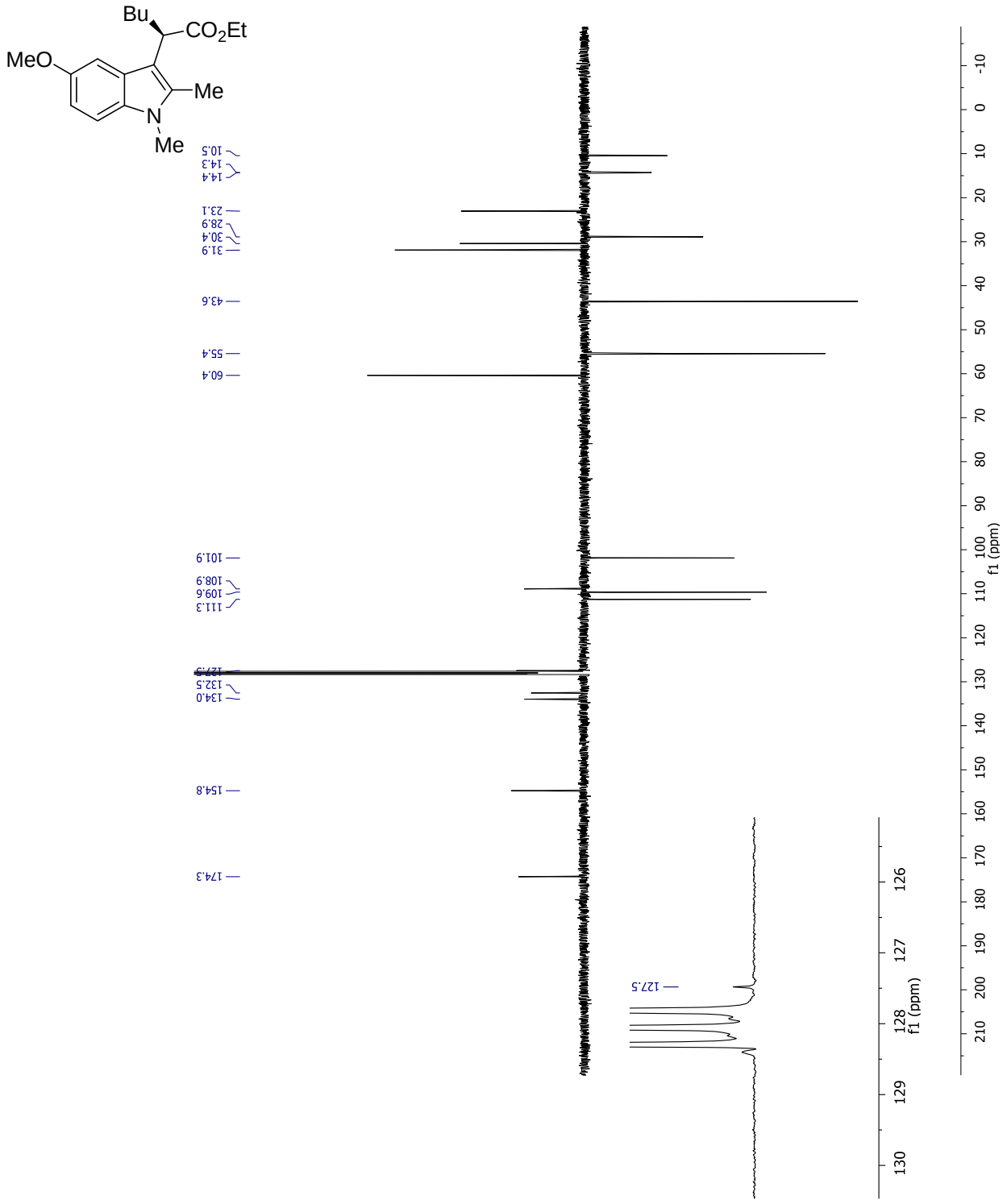
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.843	MM	0.3768	4451.98877	196.94476	98.7384
2	13.234	MM	0.3965	56.88493	2.39118	1.2616
Totals :				4508.87370	199.33594	

^{1}H NMR of 8 (400 MHz, C_6D_6)

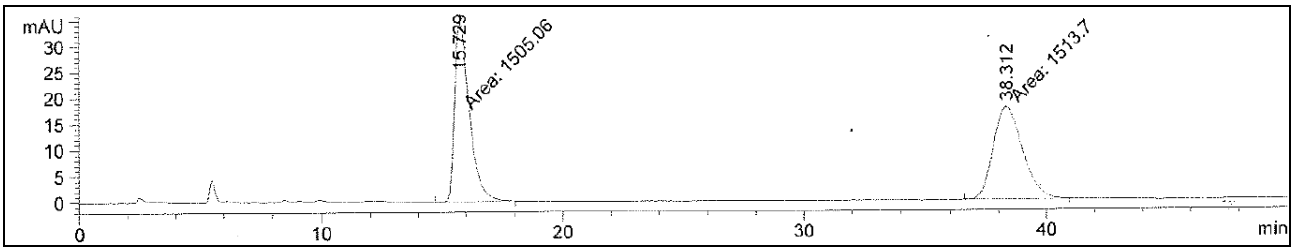




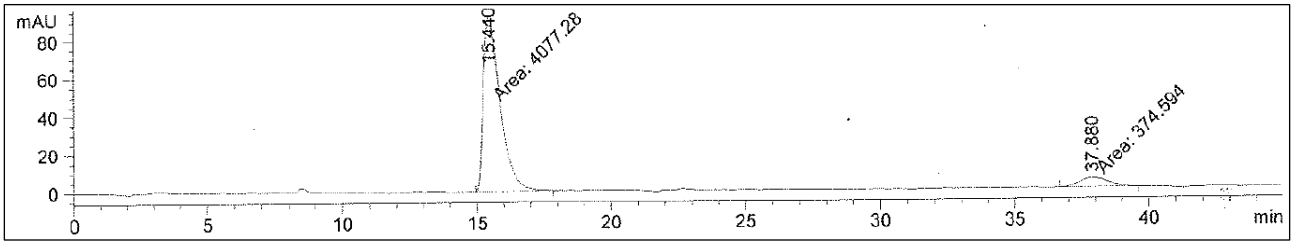
^{13}C NMR spectrum of 8 (100 MHz, C_6D_6)



HPLC resolution of racemic **8** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)



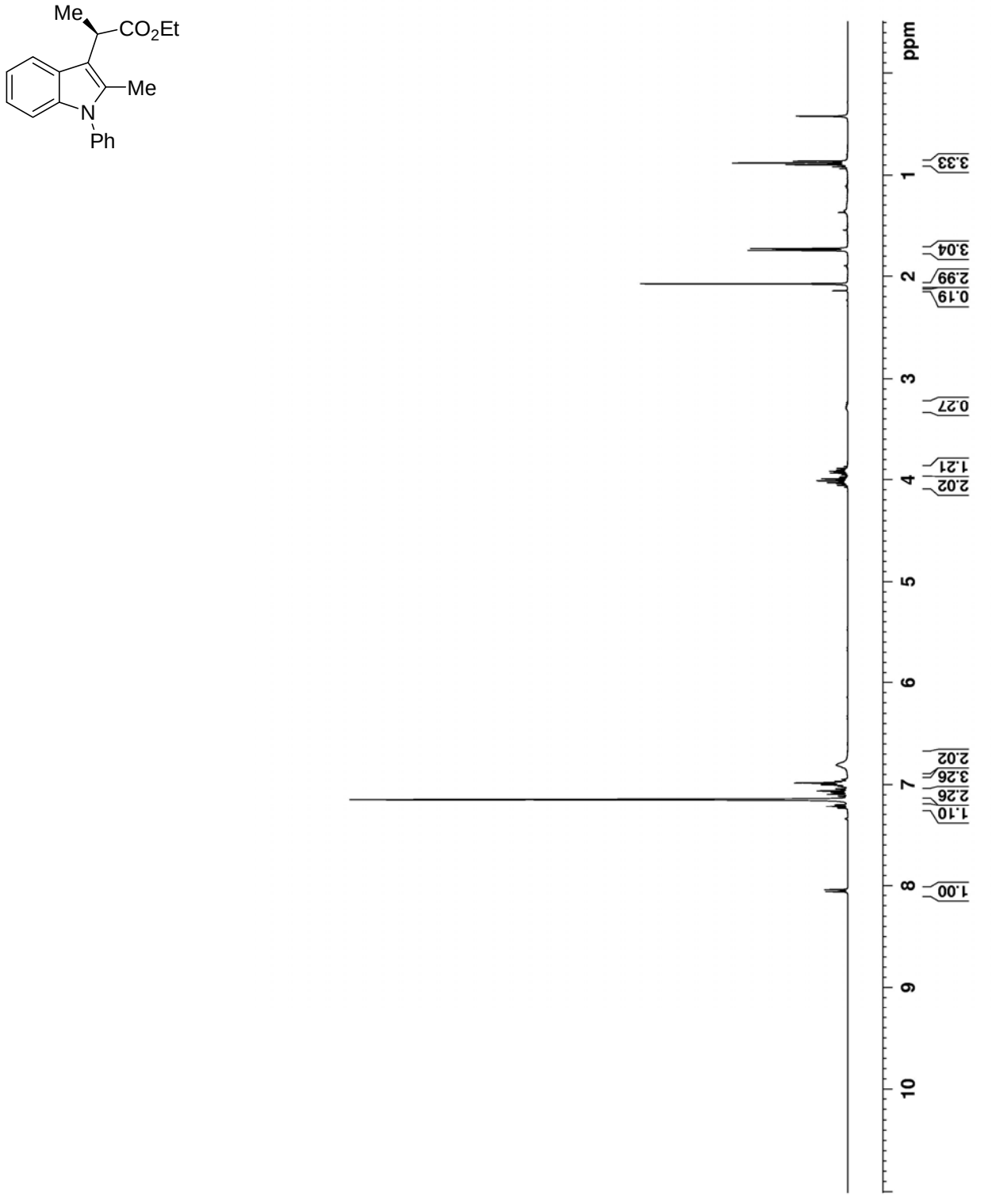
Enantiomeric excess of **8** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)



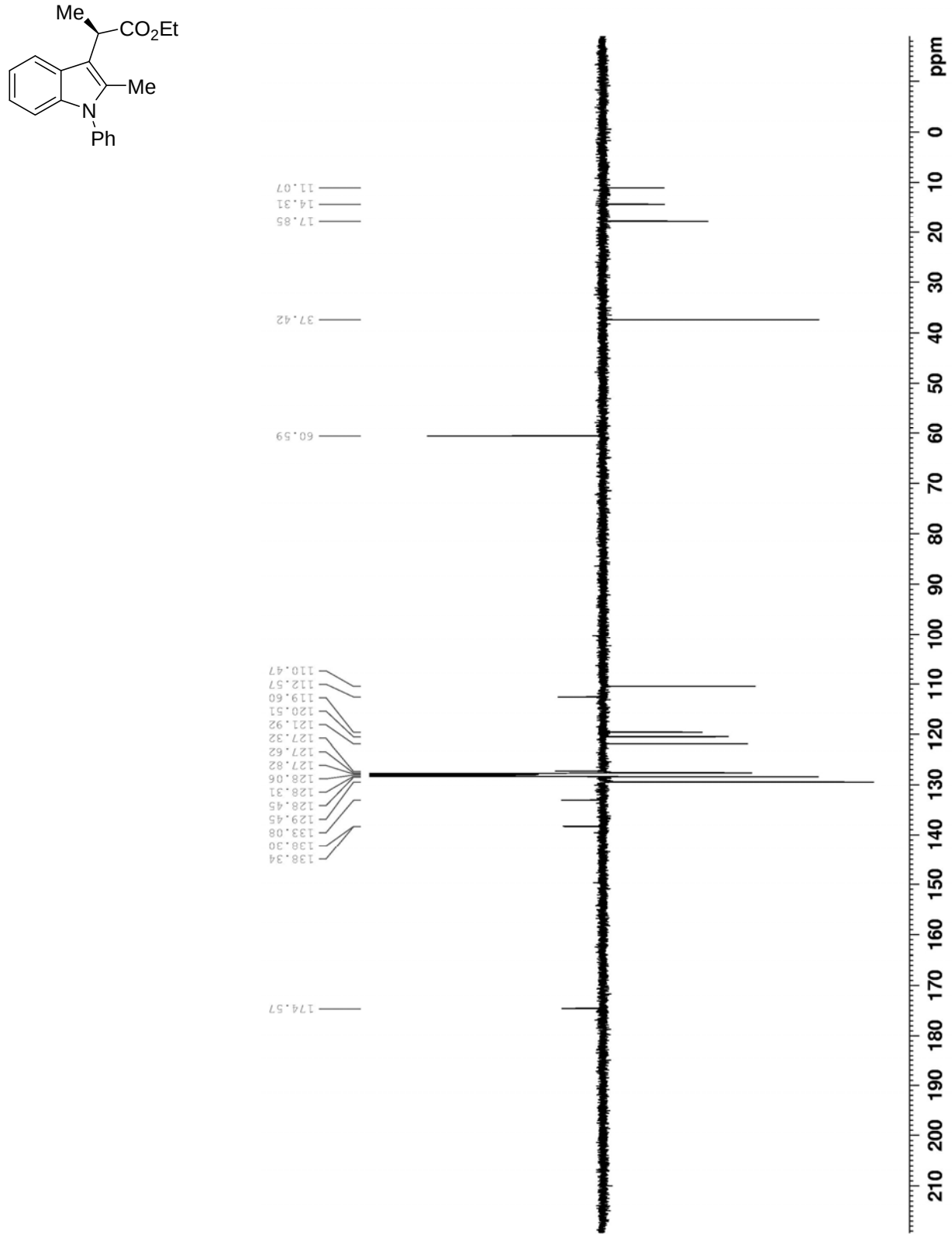
Signal 3: DAD1 C, Sig=275,4 Ref=450,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.440	MM	0.7346	4077.27930	92.50456	91.5857
2	37.880	MM	1.2845	374.59406	4.86045	8.4143
Totals :				4451.87335	97.36501	

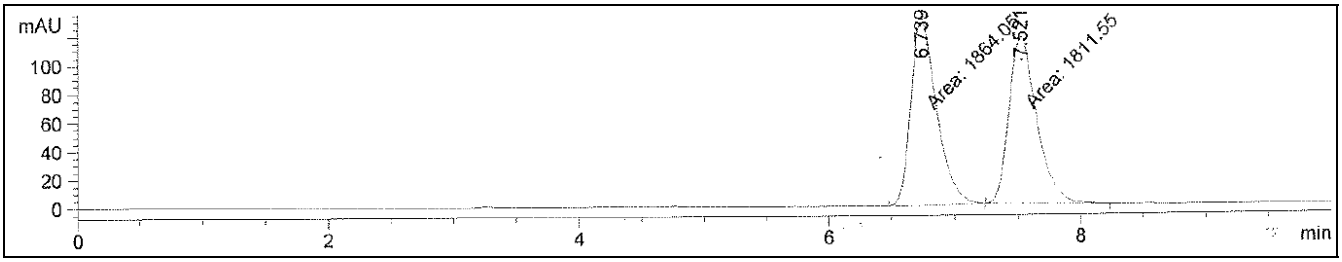
^{1}H NMR of 9 (400 MHz, C_6D_6) (94%purity)



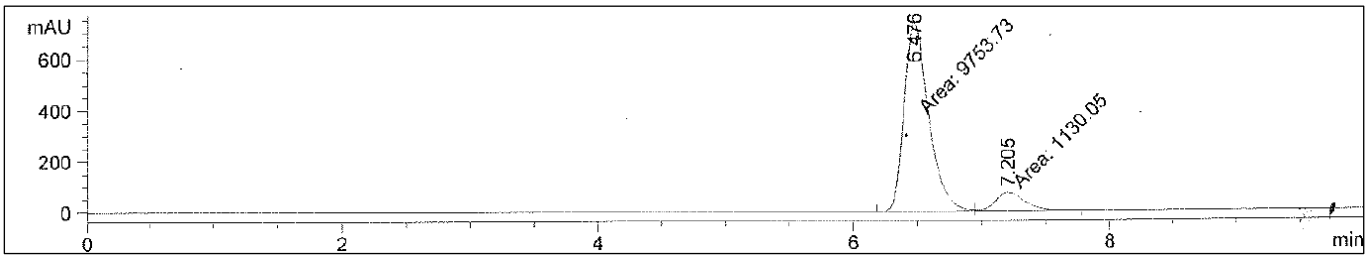
^{13}C NMR spectrum of 9 (100 MHz, C_6D_6) (94%purity)



HPLC resolution of racemic **9** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)



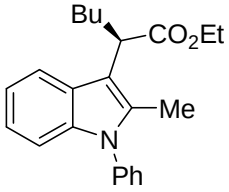
Enantiomeric excess of **9** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)

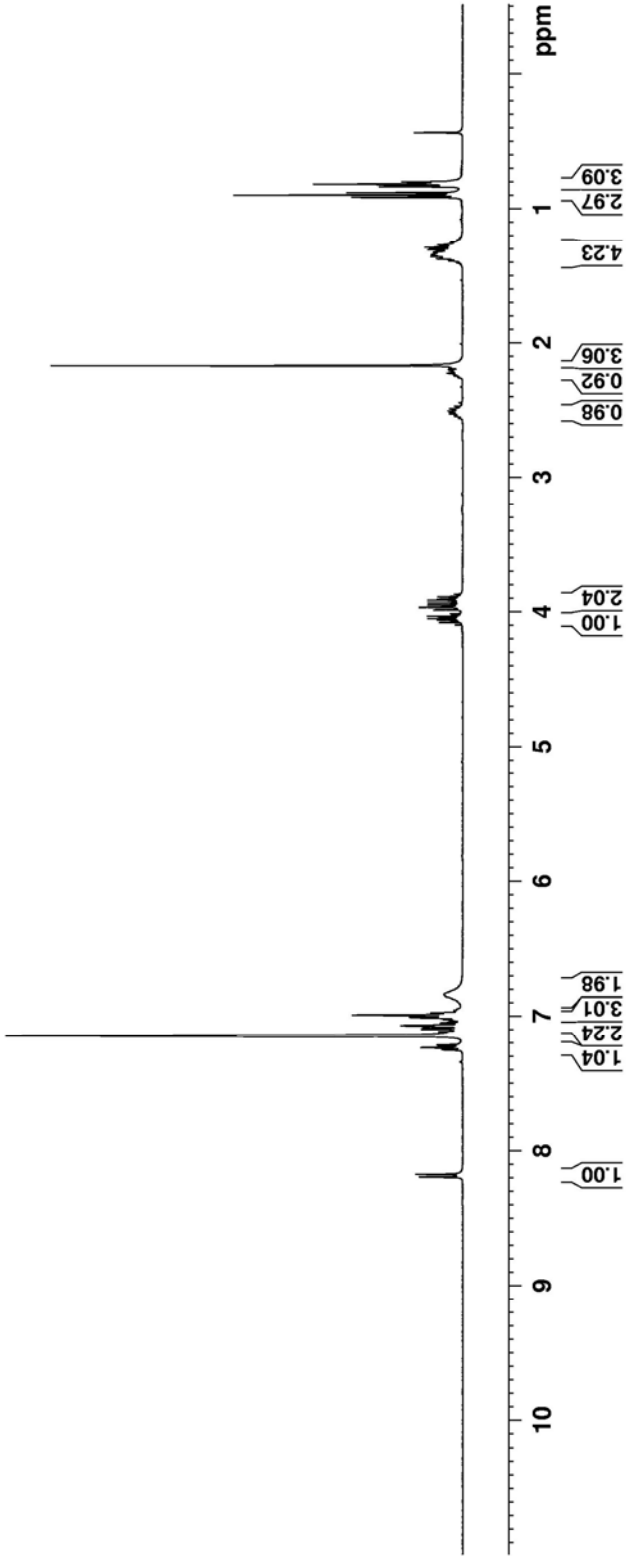


Signal 3: DAD1 C, Sig=275,4 Ref=450,80

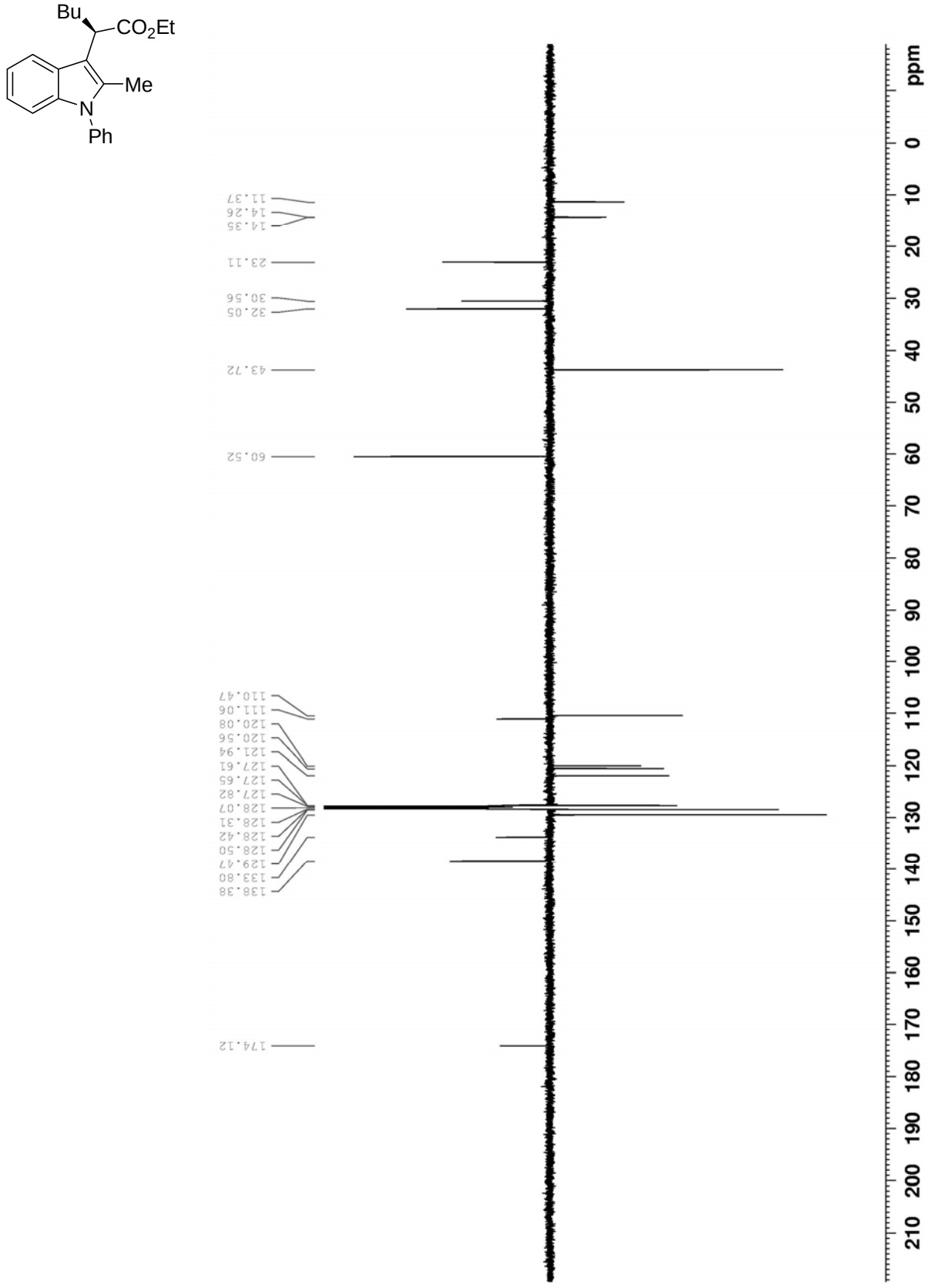
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.476	MF	0.2209	9753.73047	736.05188	89.6172
2	7.205	FM	0.2591	1130.04529	72.68864	10.3828
Totals :				1.08838e4	808.74052	

^{1}H NMR of 10 (400 MHz, C_6D_6)

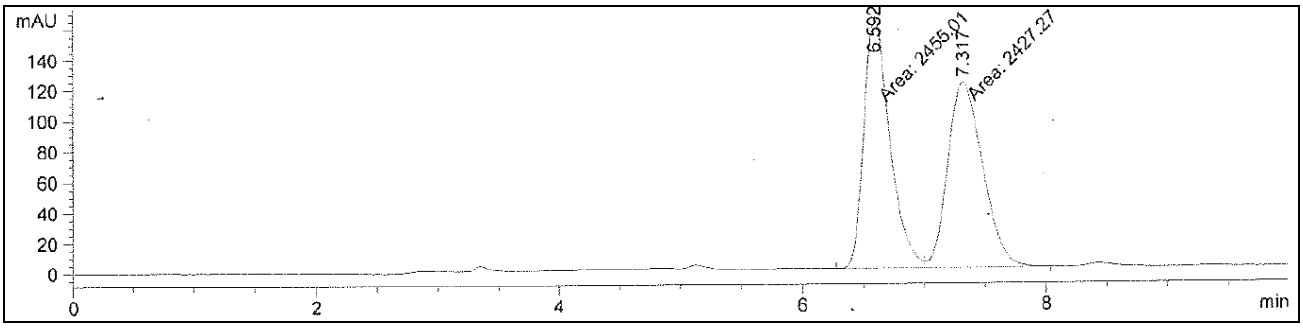




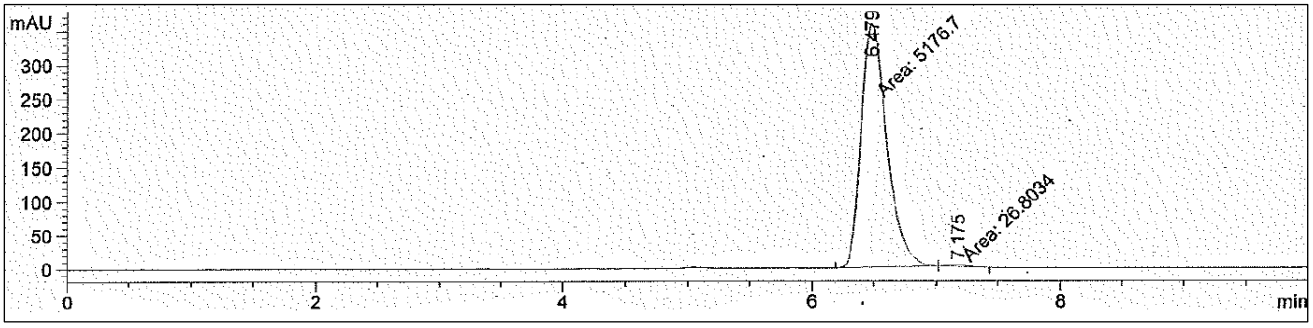
^{13}C NMR spectrum of 10 (100 MHz, C_6D_6)



HPLC resolution of racemic **10** (Chiracel OD column, 99.5:0.5 hexanes:isopropanol, 1 mL/min, 220 nm)



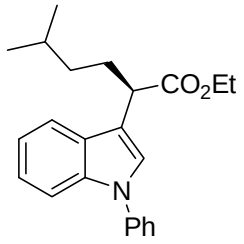
Enantiomeric excess of **10** (Chiracel OD column, 99.5:0.5 hexanes:isopropanol, 1 mL/min, 220 nm)

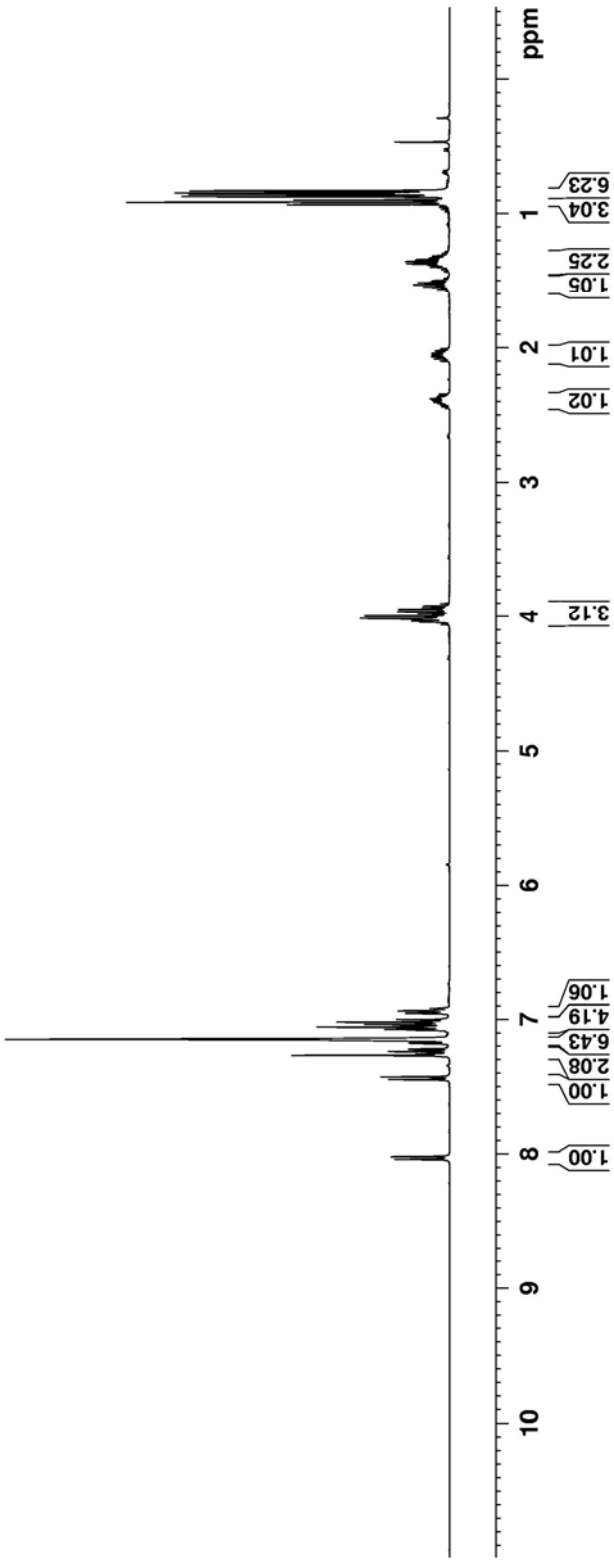


Signal 2: DAD1 B, Sig=220,4 Ref=450,80

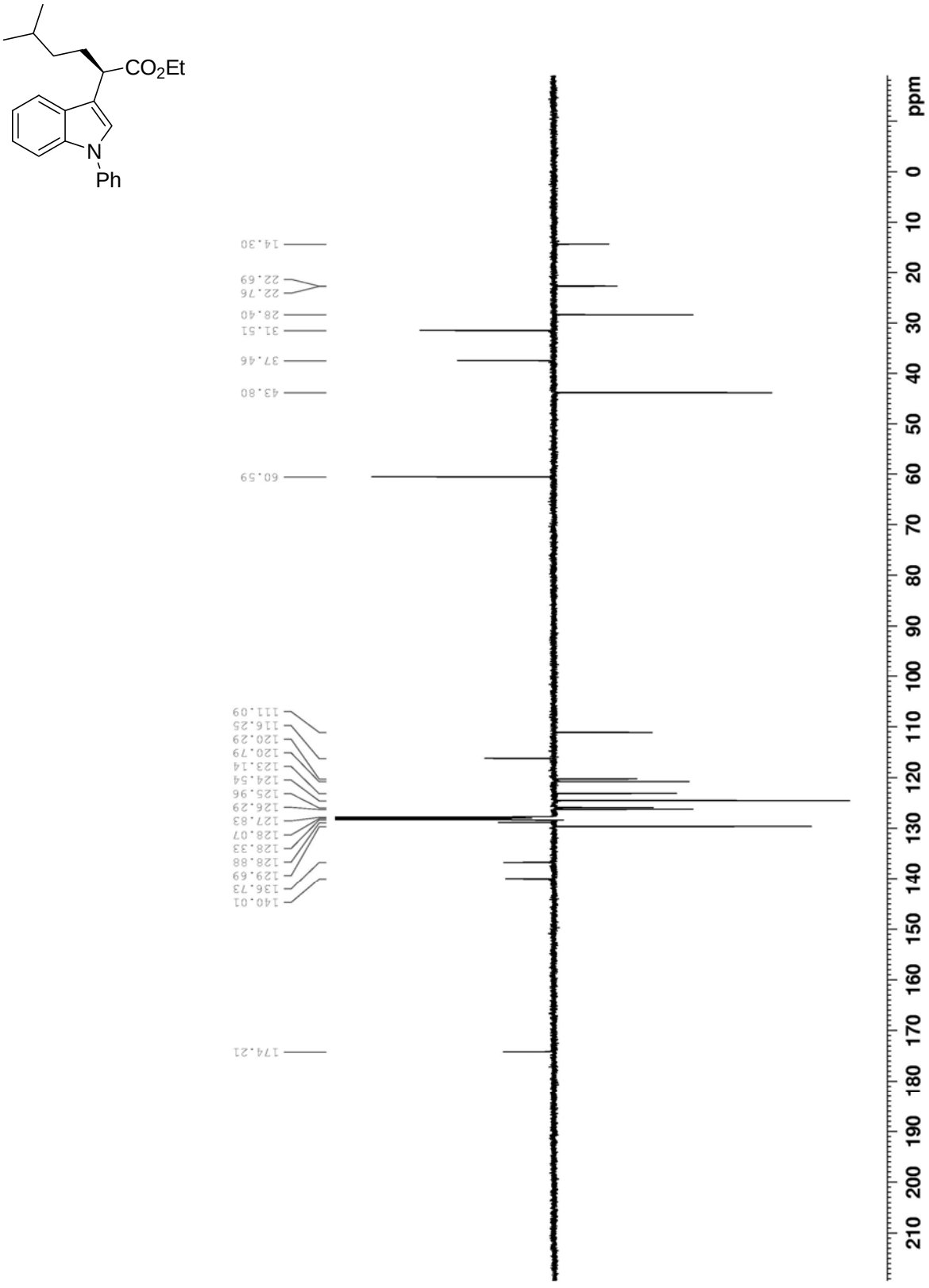
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.479	MM	0.2403	5176.70264	359.05667	99.4849
2	7.175	MM	0.1988	26.80336	2.24681	0.5151
Totals :				5203.50599	361.30348	

^{1}H NMR of 11 (400 MHz, C_6D_6)



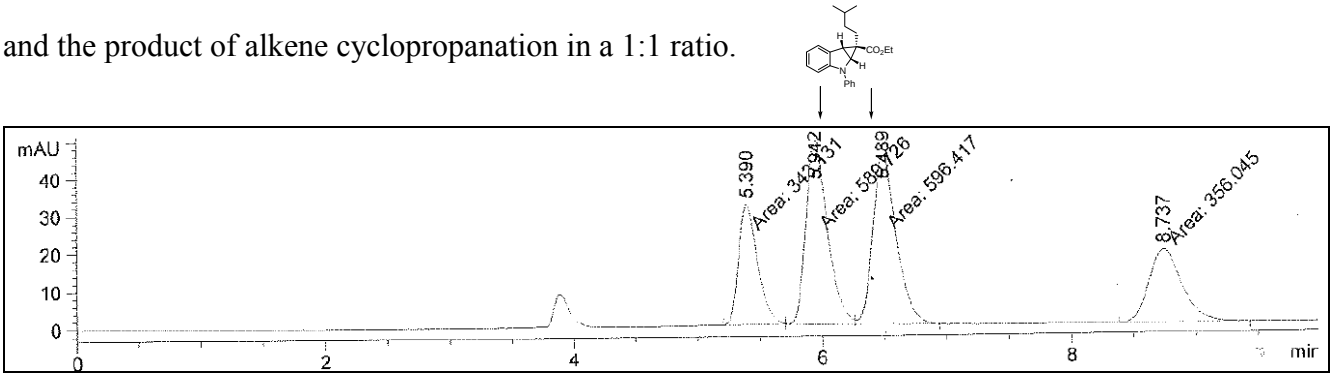


^{13}C NMR spectrum of 11 (100 MHz, C_6D_6)

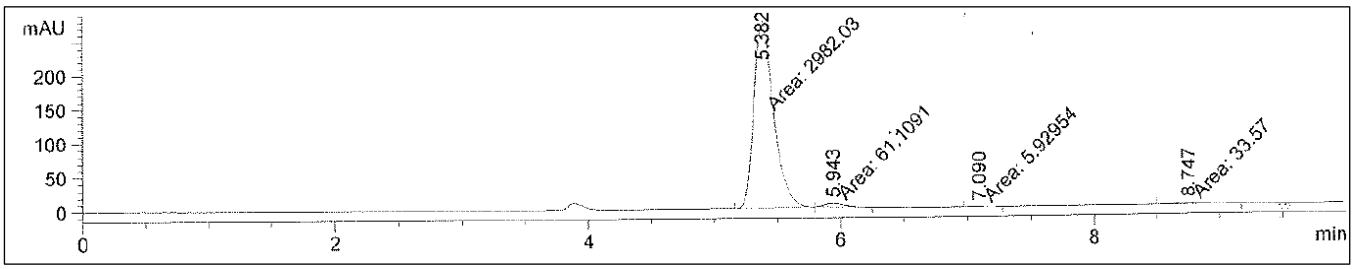


HPLC resolution of racemic **11** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)

NOTE: Preparation of racemic **11** using Rh_2Piv_4 gave the indole C-H functionalization product and the product of alkene cyclopropanation in a 1:1 ratio.



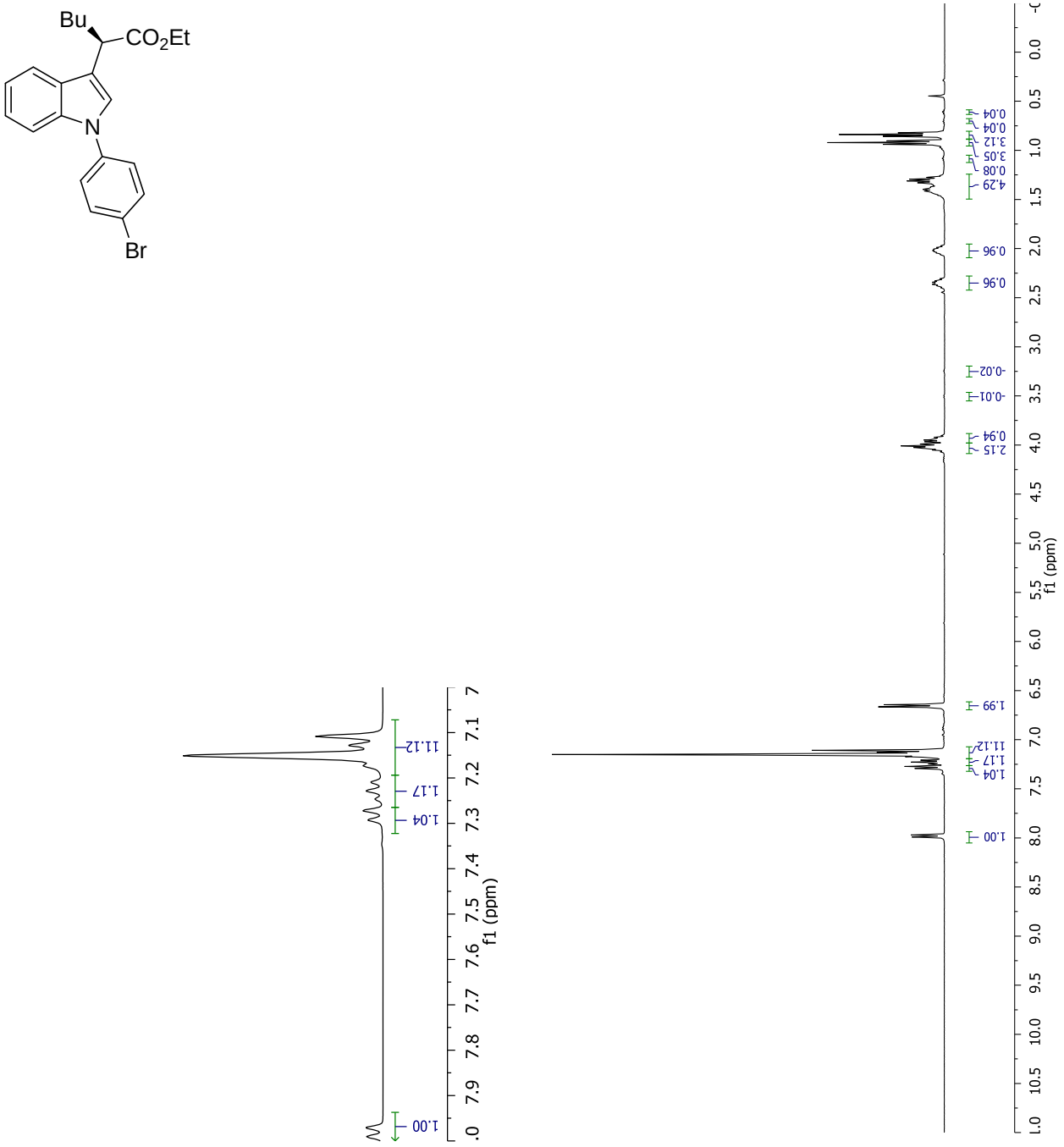
Enantiomeric excess of **11** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)



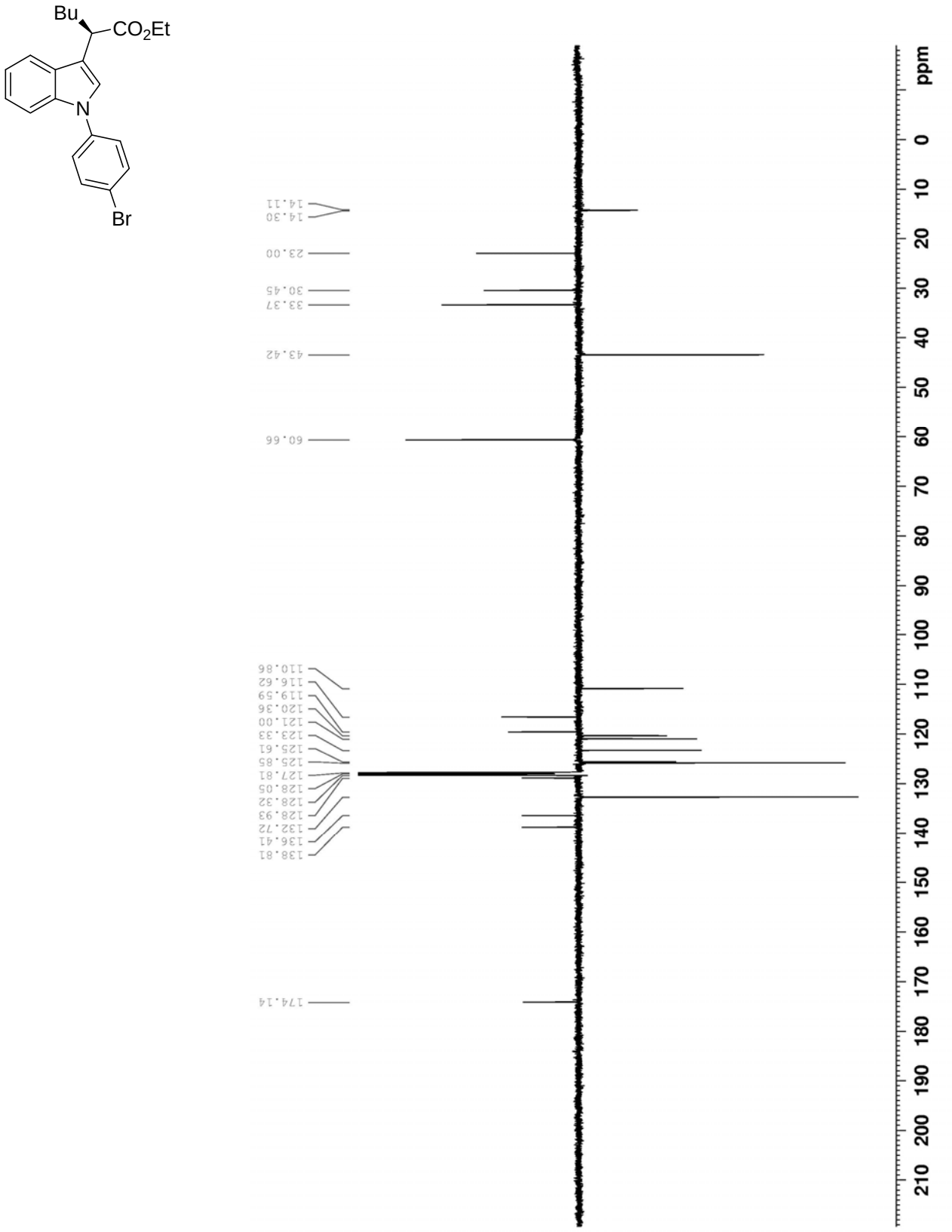
Signal 3: DAD1 C, Sig=275,4 Ref=450,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.382	MM	0.1792	2982.02515	277.29205	96.7363
2	5.943	MM	0.1815	61.10906	5.61121	1.9824
3	7.090	MM	0.1791	5.92954	5.51896e-1	0.1924
4	8.747	MM	0.2943	33.57003	1.90101	1.0890
Totals :				3082.63377	285.35616	

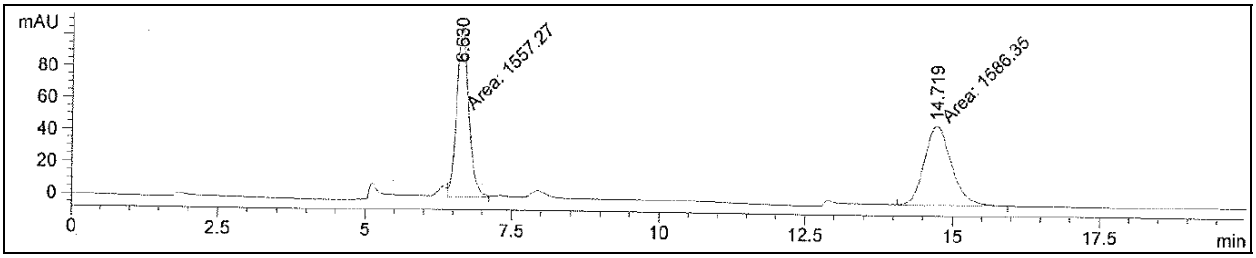
^{1}H NMR of 12 (400 MHz, C_6D_6) (95% purity)



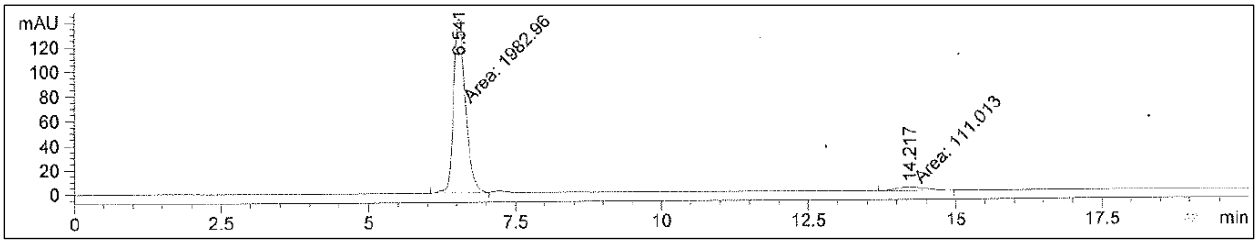
^{13}C NMR spectrum of 12 (100 MHz, C_6D_6) (95% purity)



HPLC resolution of racemic **12** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)



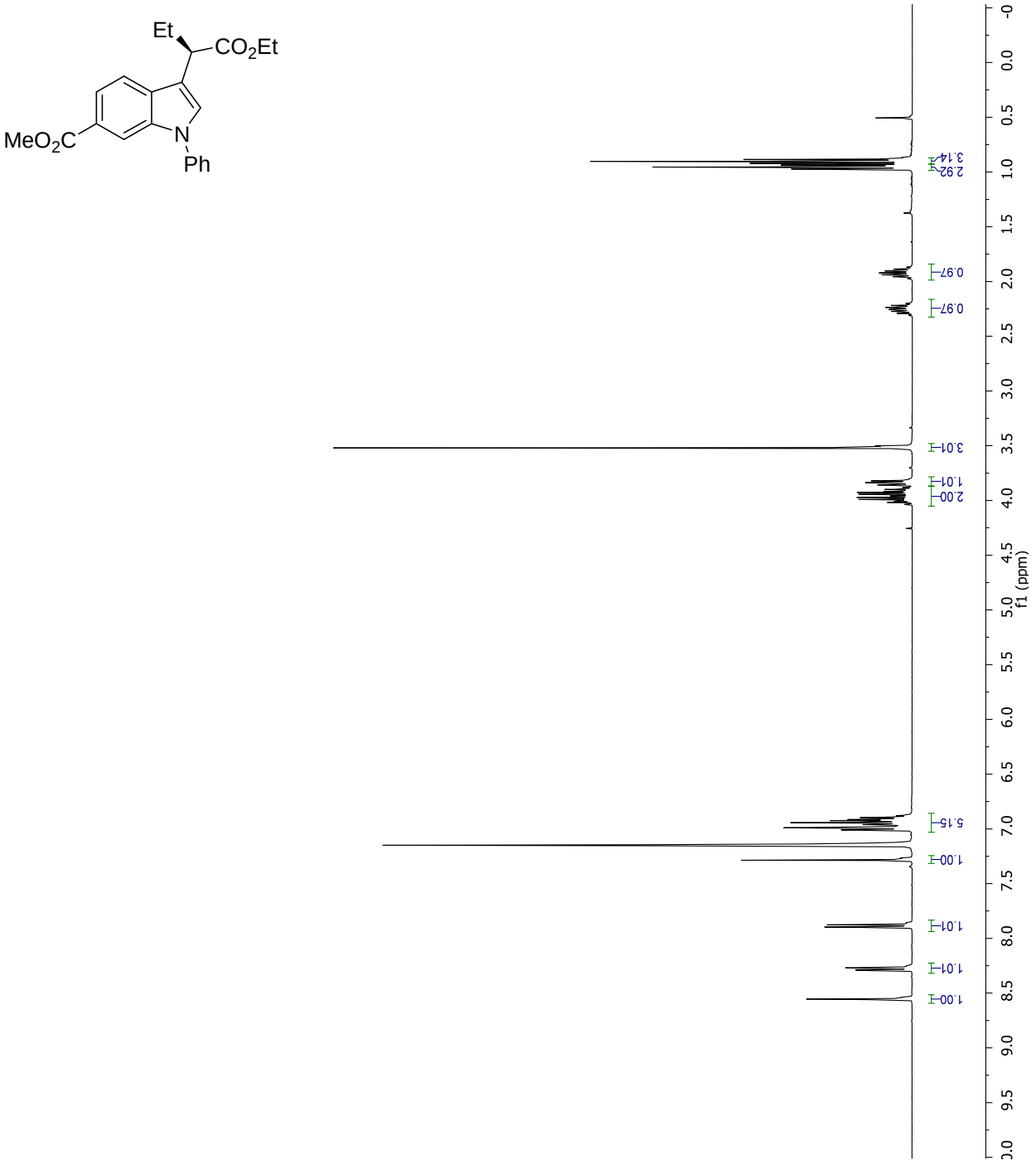
Enantiomeric excess of **12** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)



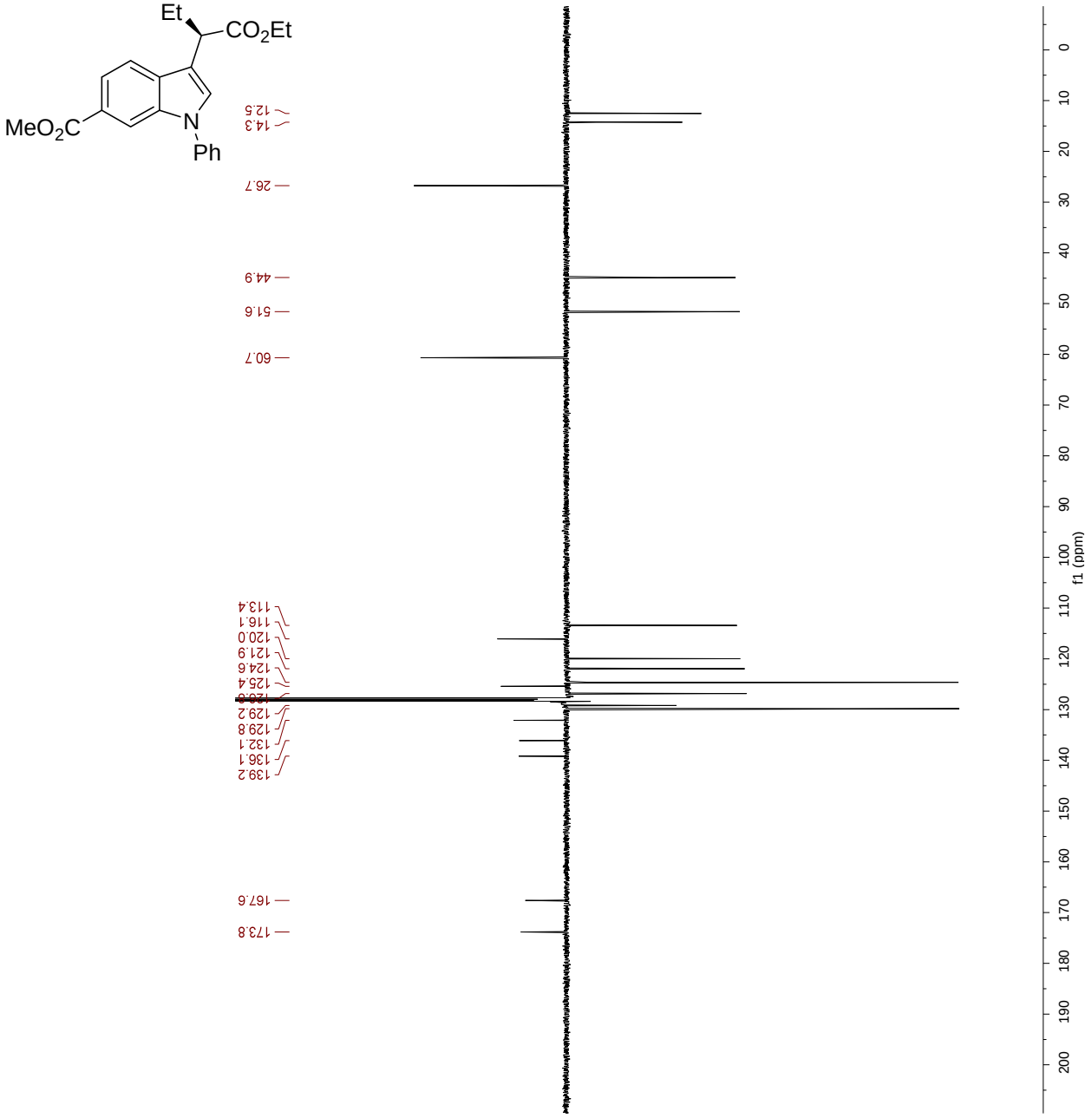
Signal 3: DAD1 C, Sig=275,4 Ref=450,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.541	MM	0.2328	1982.95935	141.97328	94.6985
2	14.217	MM	0.5351	111.01264	3.45758	5.3015
Totals :				2093.97199	145.43086	

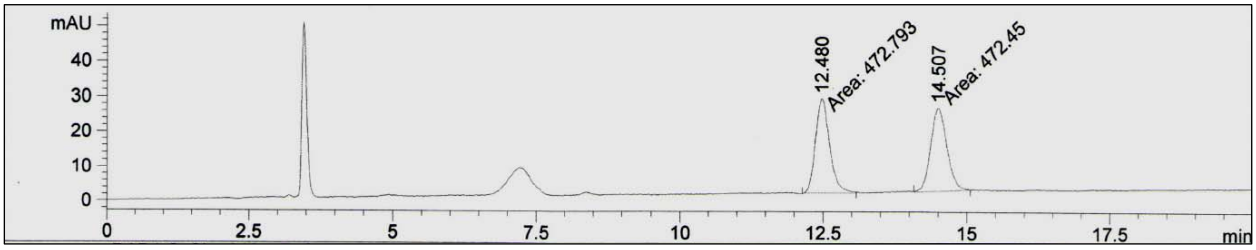
^{1}H NMR of 13 (400 MHz, C_6D_6)



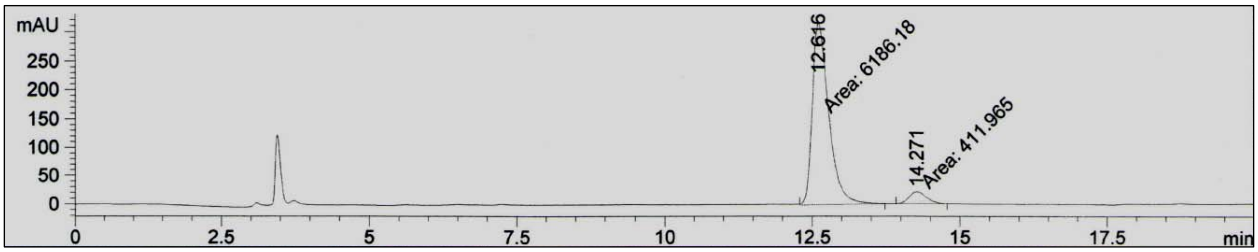
^{13}C NMR of 13 (100 MHz, C_6D_6)



HPLC resolution of racemic **13** (Chiracel IA column, 99:1 hexanes:isopropanol, 1 mL/min, 220 nm)



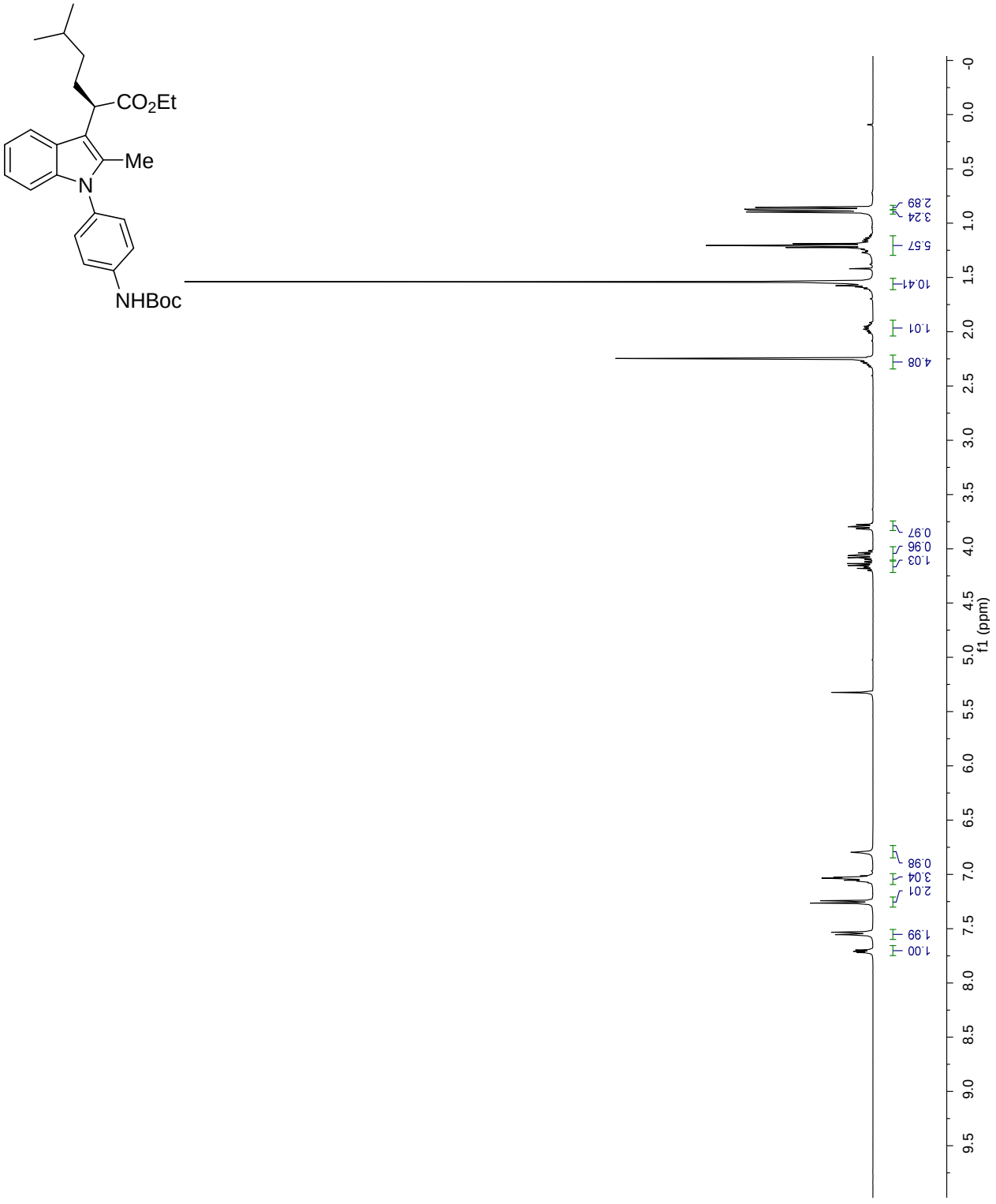
Enantiomeric excess of **13** (Chiracel IA column, 99:1 hexanes:isopropanol, 1 mL/min, 220 nm)



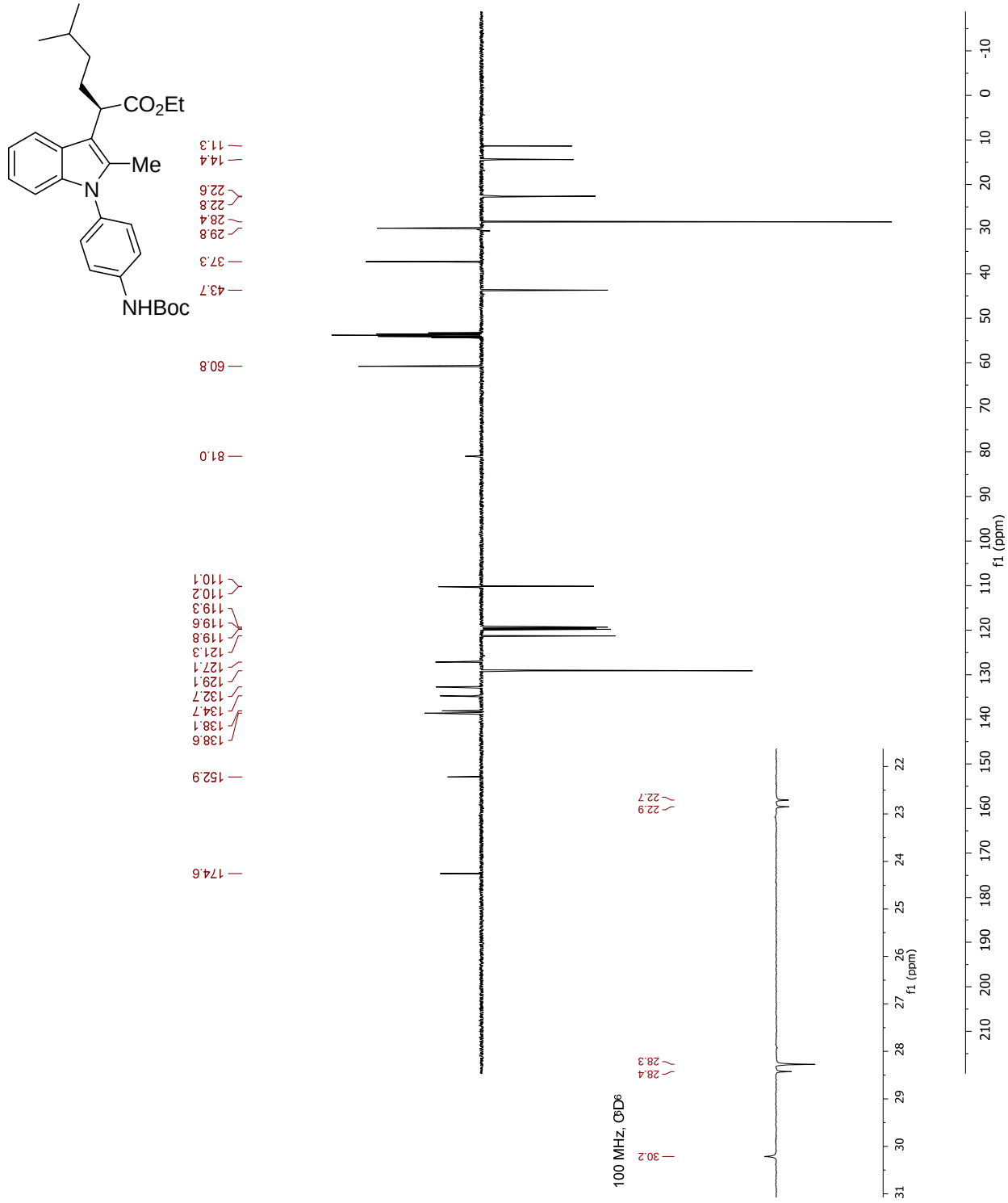
Signal 2: DAD1 B, Sig=220,4 Ref=450,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.616	MM	0.3276	6186.17871	314.73395	93.7563
2	14.271	MM	0.3407	411.96527	20.15228	6.2437
Totals :				6598.14398	334.88623	

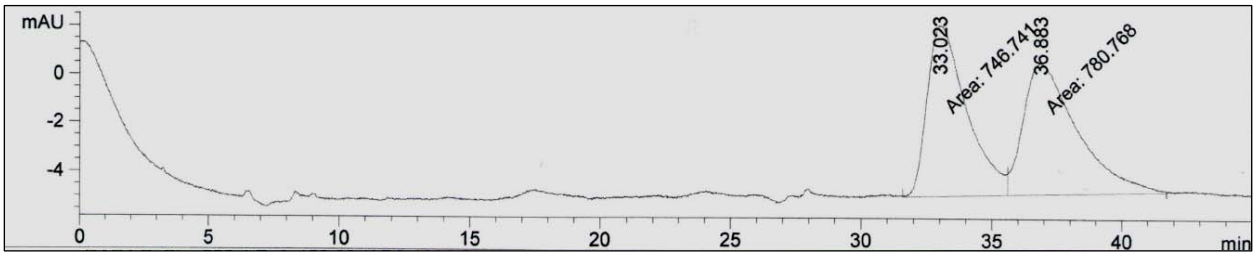
^{1}H NMR of 14 (400 MHz, CD_2Cl_2)



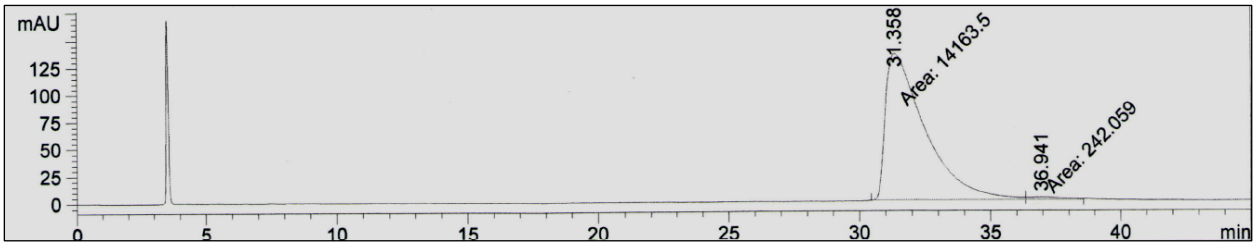
^{13}C NMR of 14 (100 MHz, CD_2Cl_2)



HPLC resolution of racemic **14** (Chiracel IA column, 99.5:0.5 hexanes:isopropanol, 1 mL/min, 254 nm)



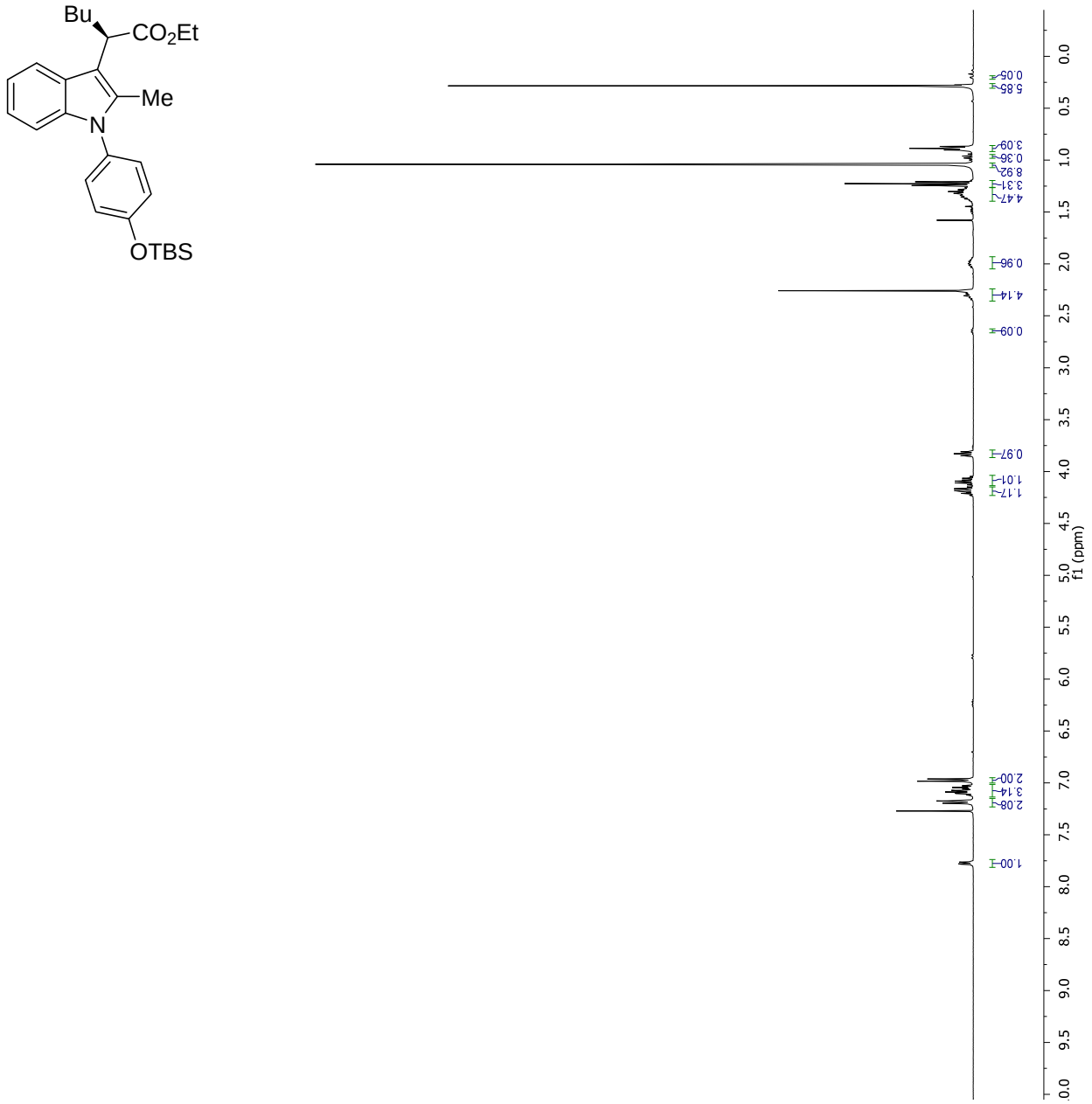
Enantiomeric excess of **14** (Chiracel IA column, 99.5:0.5 hexanes:isopropanol, 1 mL/min, 254 nm)



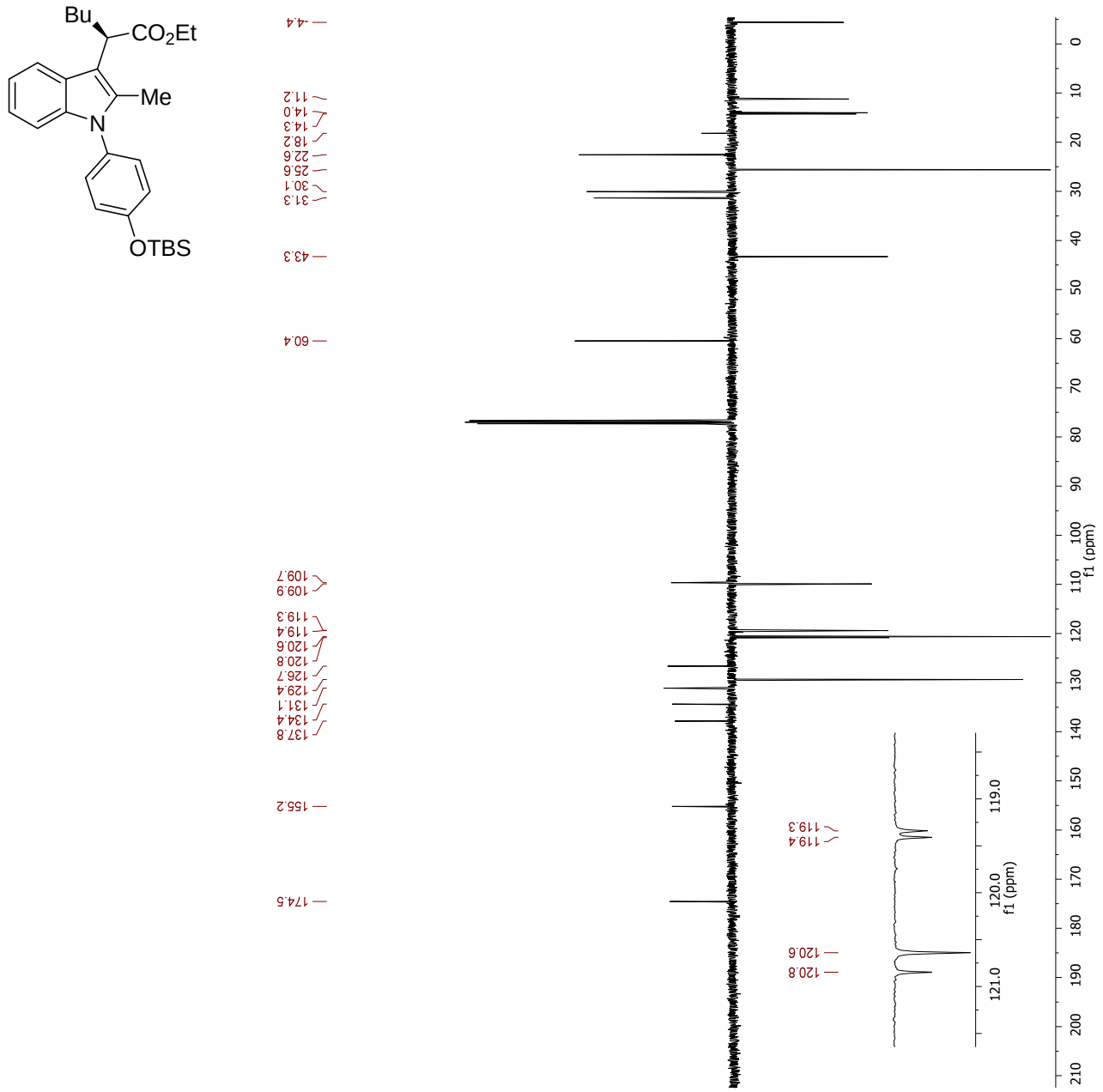
Signal 1: DAD1 A, Sig=254,4 Ref=450,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.358	MF	1.7554	1.41635e4	134.47302	98.3197
2	36.941	FM	1.6238	242.05911	2.48448	1.6803
Totals :				1.44056e4	136.95750	

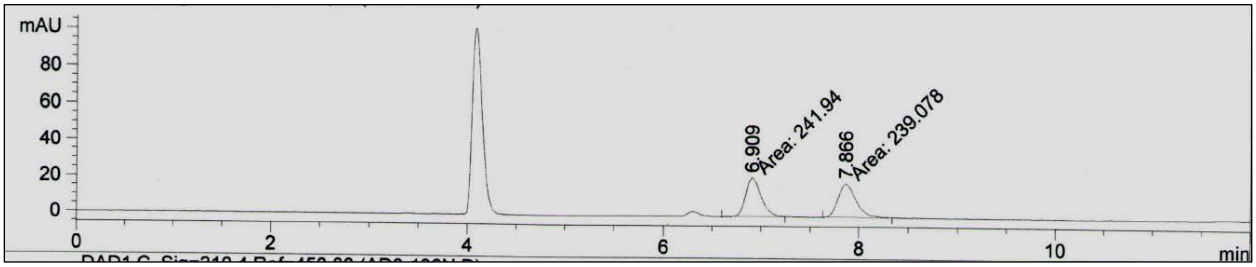
^{1}H NMR of 15 (400 MHz, $CDCl_3$) (90% purity)



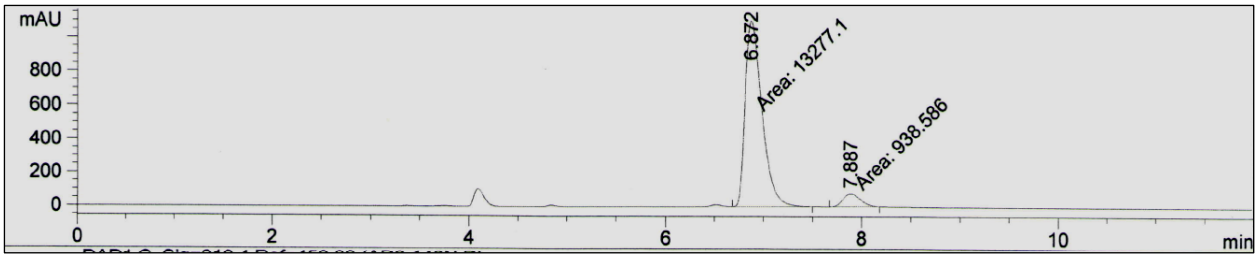
^{13}C NMR of 15 (100 MHz, $CDCl_3$) (90% purity)



HPLC resolution of racemic **15** (Chiracel IB column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)



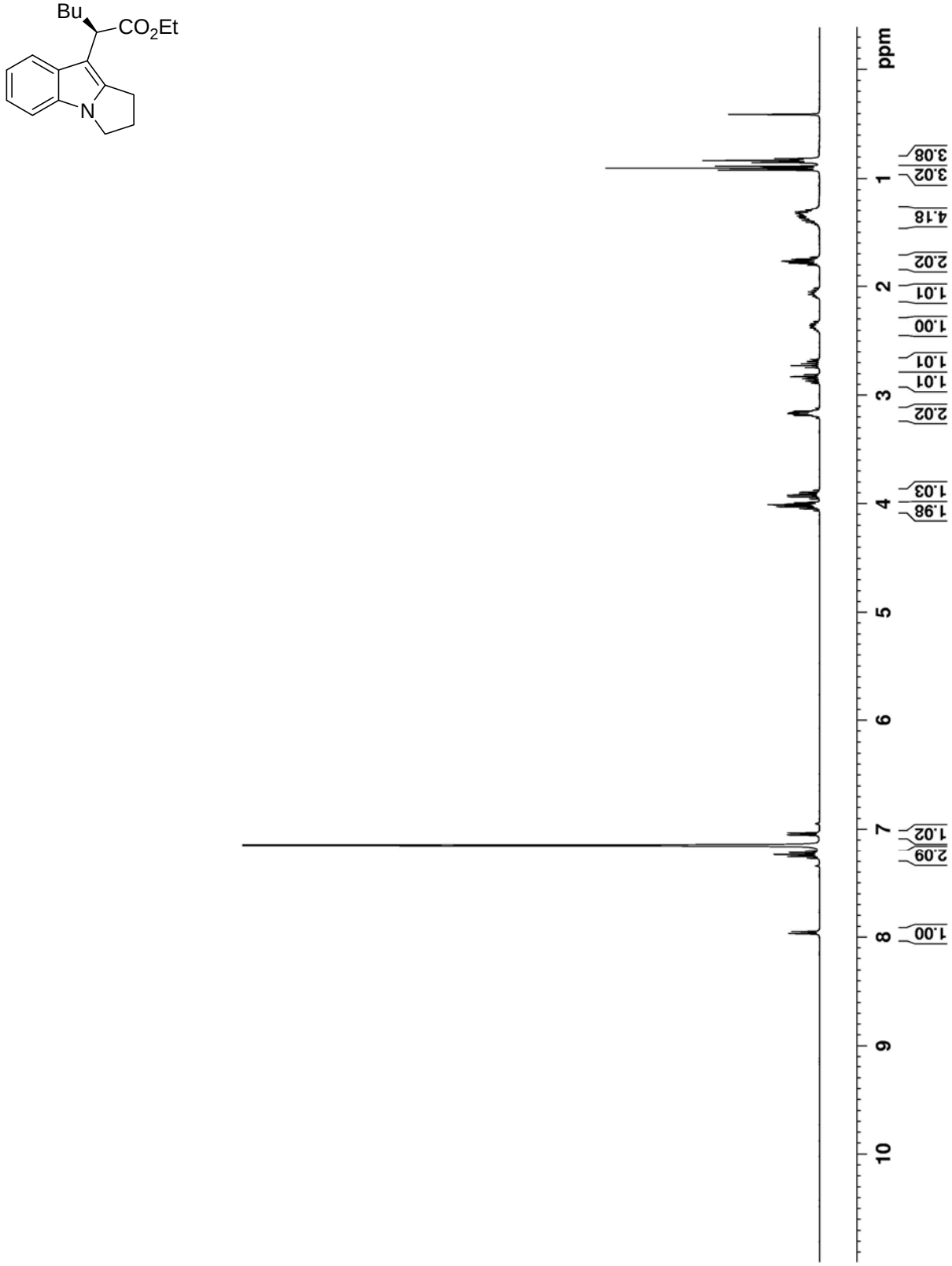
Enantiomeric excess of **15** (Chiracel IB column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)



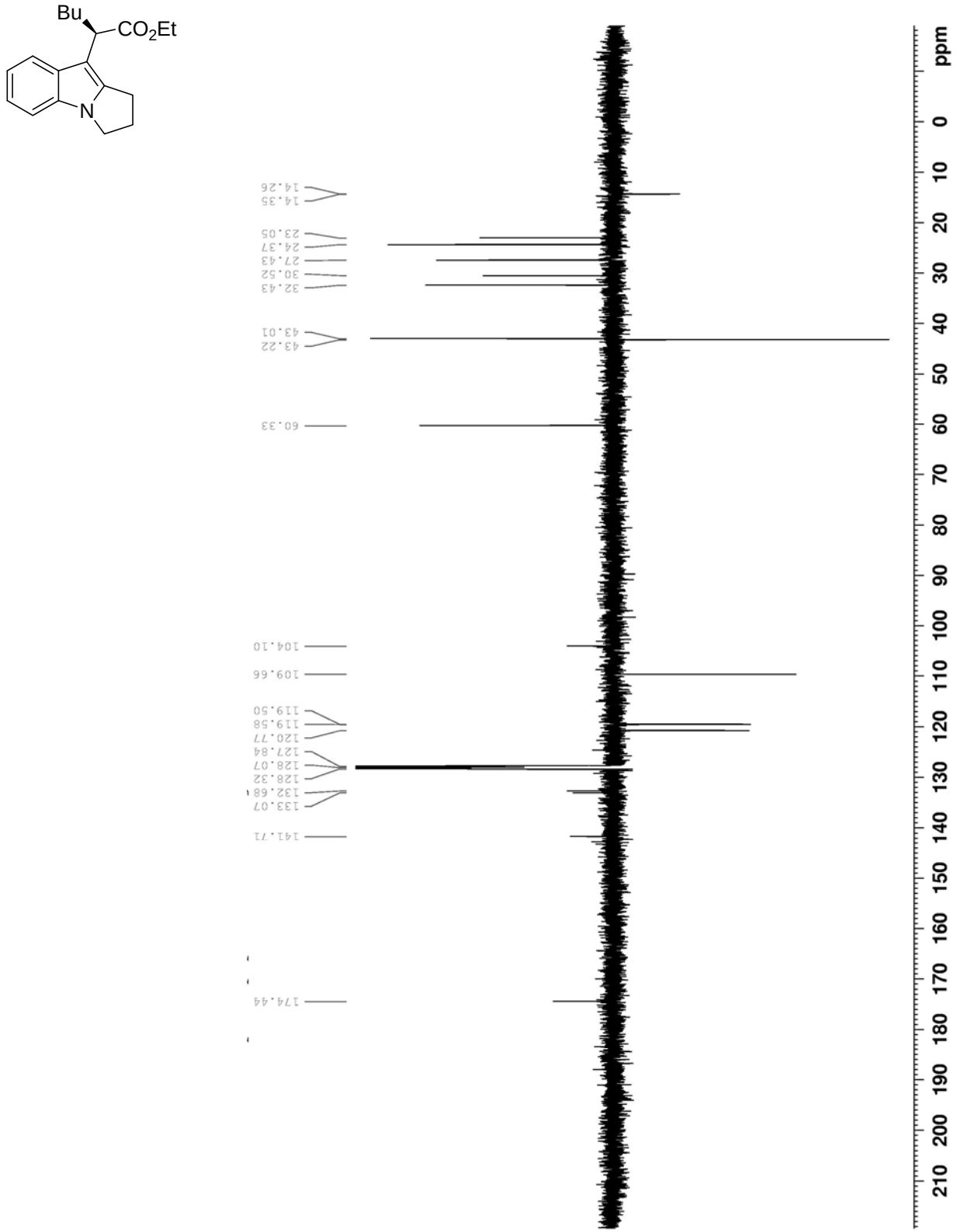
Signal 2: DAD1 B, Sig=220,4 Ref=450,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.872	MM	0.1996	1.32771e4	1108.56372	93.3975
2	7.887	MM	0.2029	938.58588	77.09678	6.6025
Totals :				1.42157e4	1185.66050	

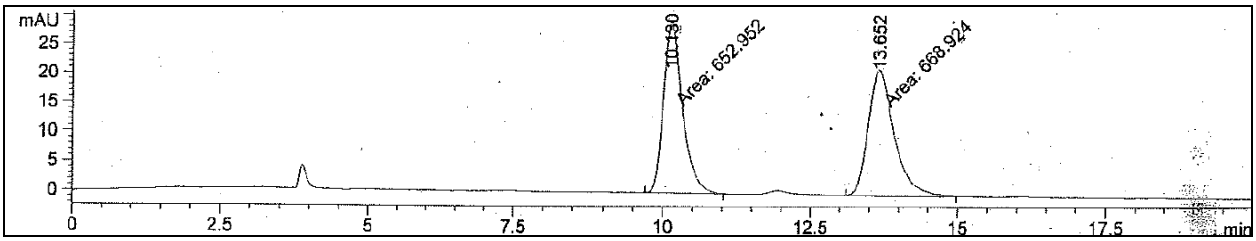
^{1}H NMR of 16 (400 MHz, C_6D_6)



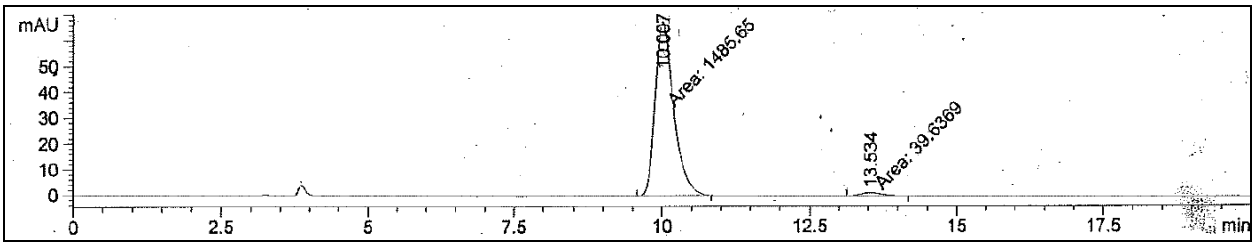
^{13}C NMR spectrum of 16 (100 MHz, C_6D_6)



HPLC resolution of racemic **16** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)



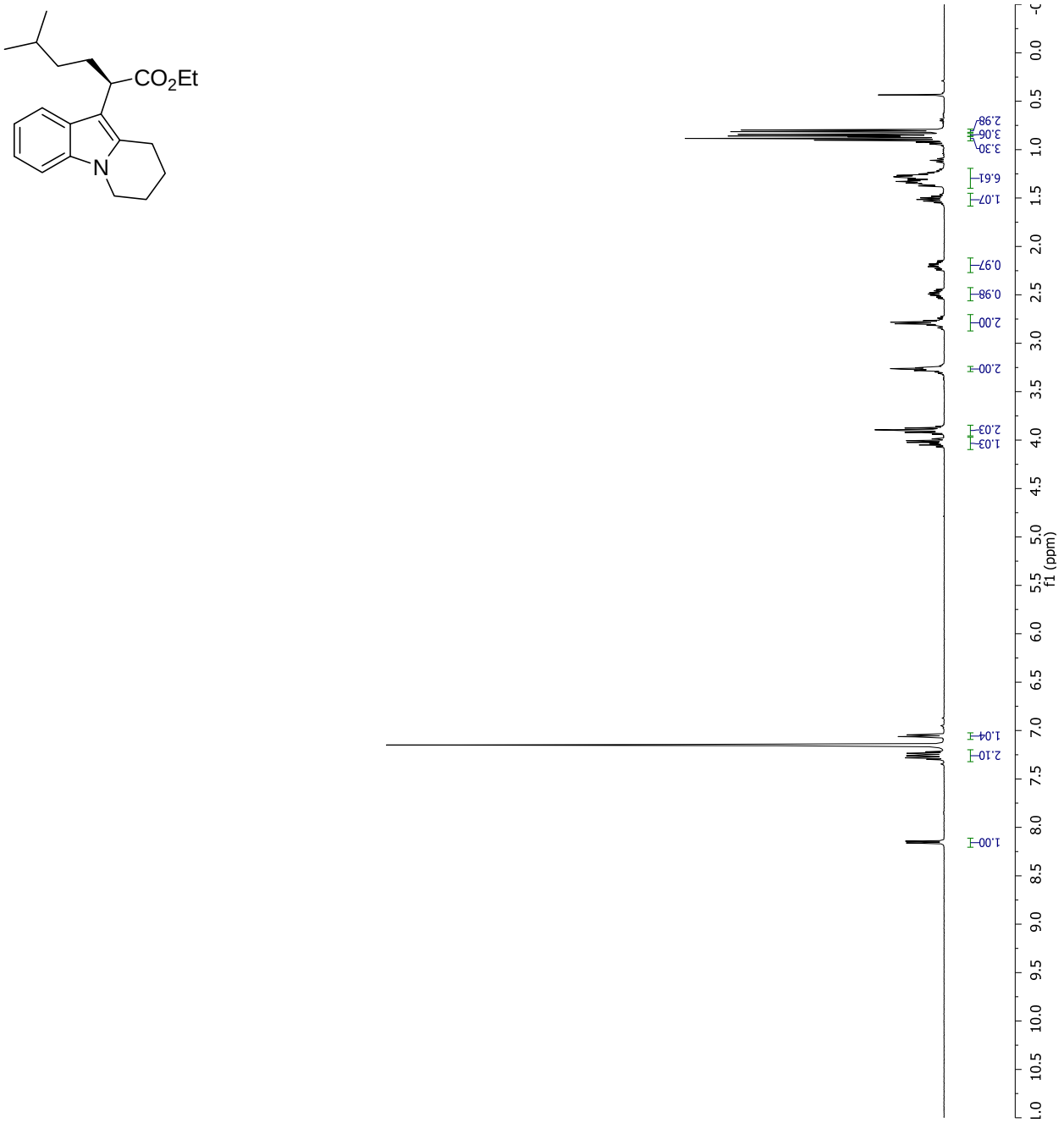
Enantiomeric excess of **16** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 275 nm)



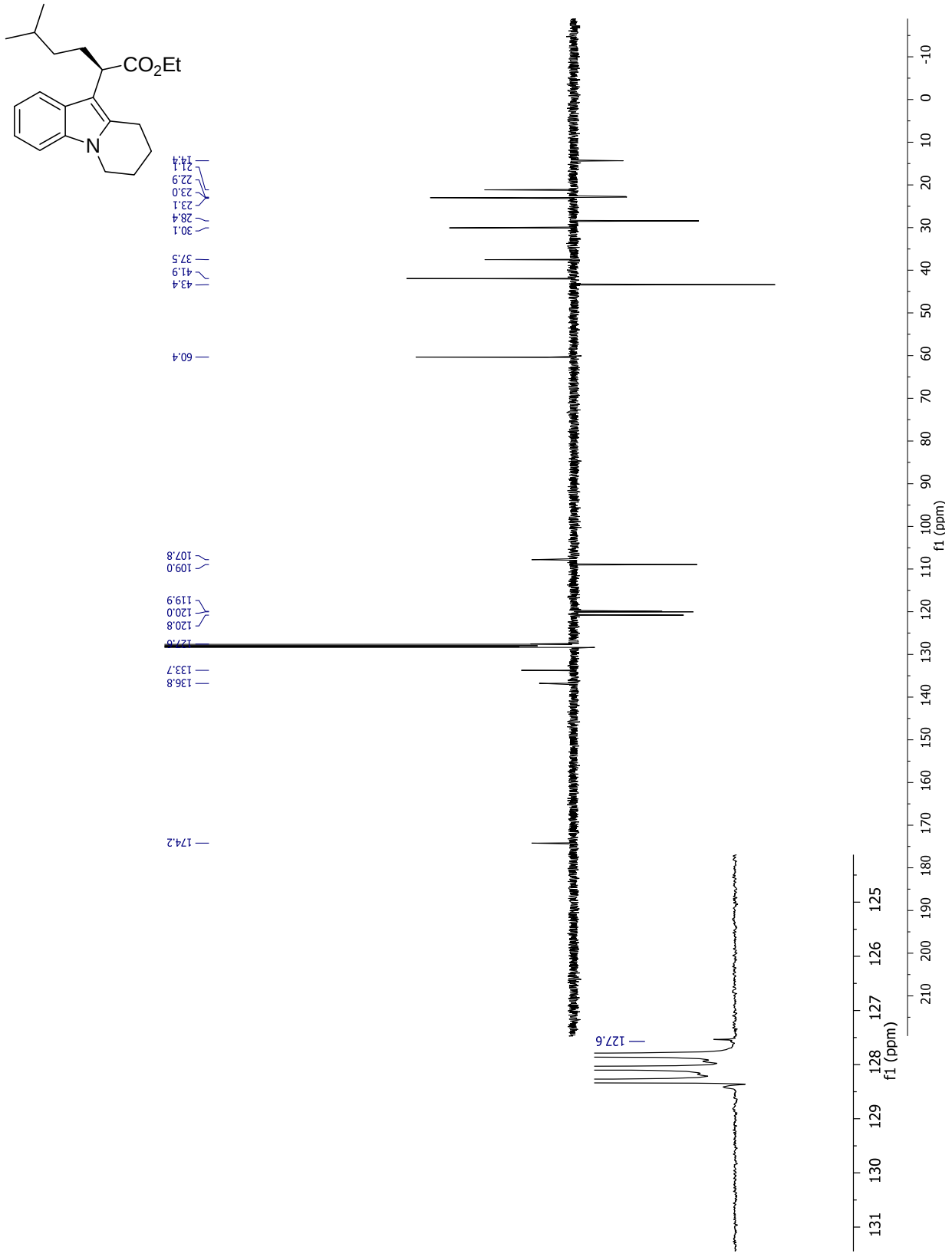
Signal 3: DAD1 C, Sig=275,4 Ref=450,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.007	MM	0.3649	1485.65308	67.86433	97.4014
2	13.534	MM	0.4672	39.63686	1.41397	2.5986
Totals :				1525.28994	69.27830	

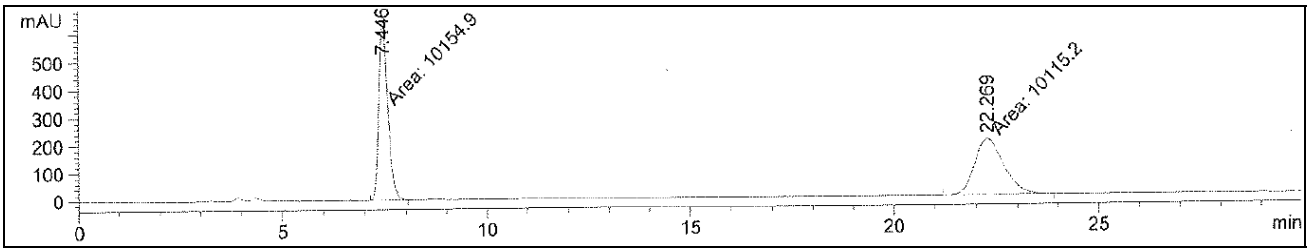
^{1}H NMR of 17 (400 MHz, C_6D_6)



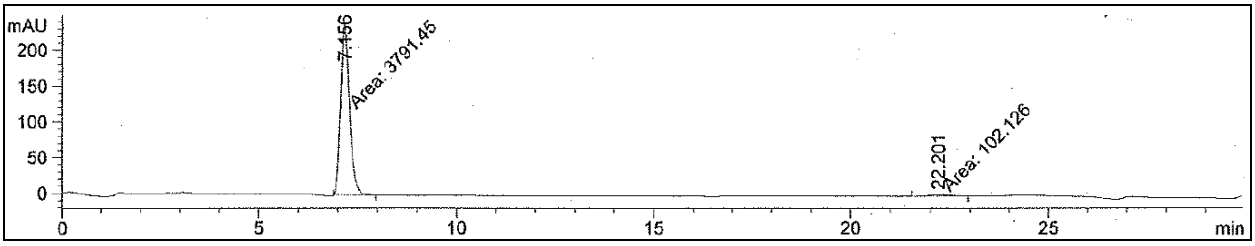
^{13}C NMR spectrum of 17 (100 MHz, C_6D_6)



HPLC resolution of racemic **17** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 220 nm)

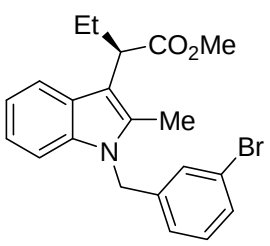


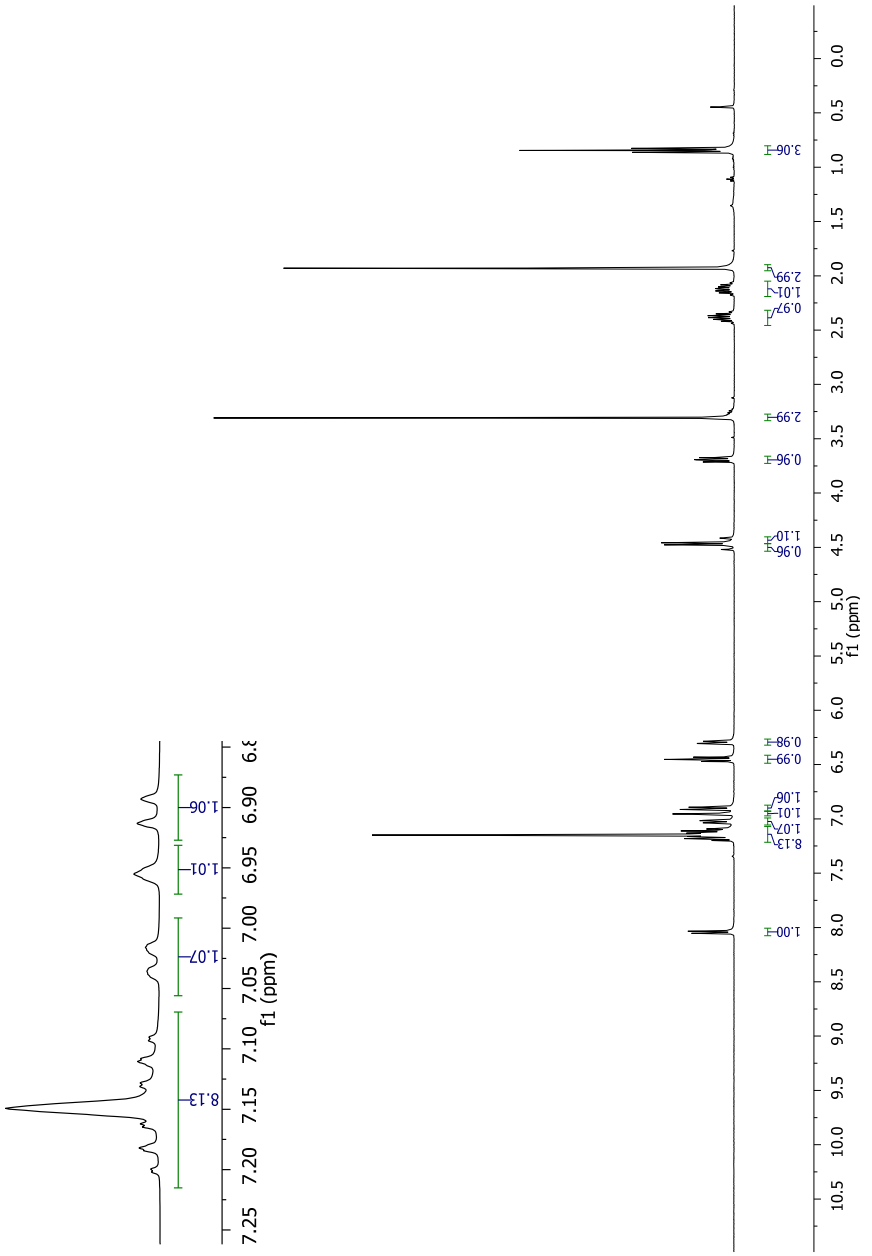
Enantiomeric excess of **17** (Chiracel OD column, 99:1 hexanes:isopropanol, 1 mL/min, 220 nm)



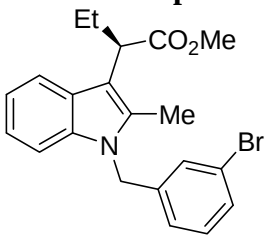
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.156	MM	0.2638	3791.44629	239.56104	97.3771
2	22.201	MM	0.7685	102.12646	2.21475	2.6229
Totals :				3893.57275	241.77578	

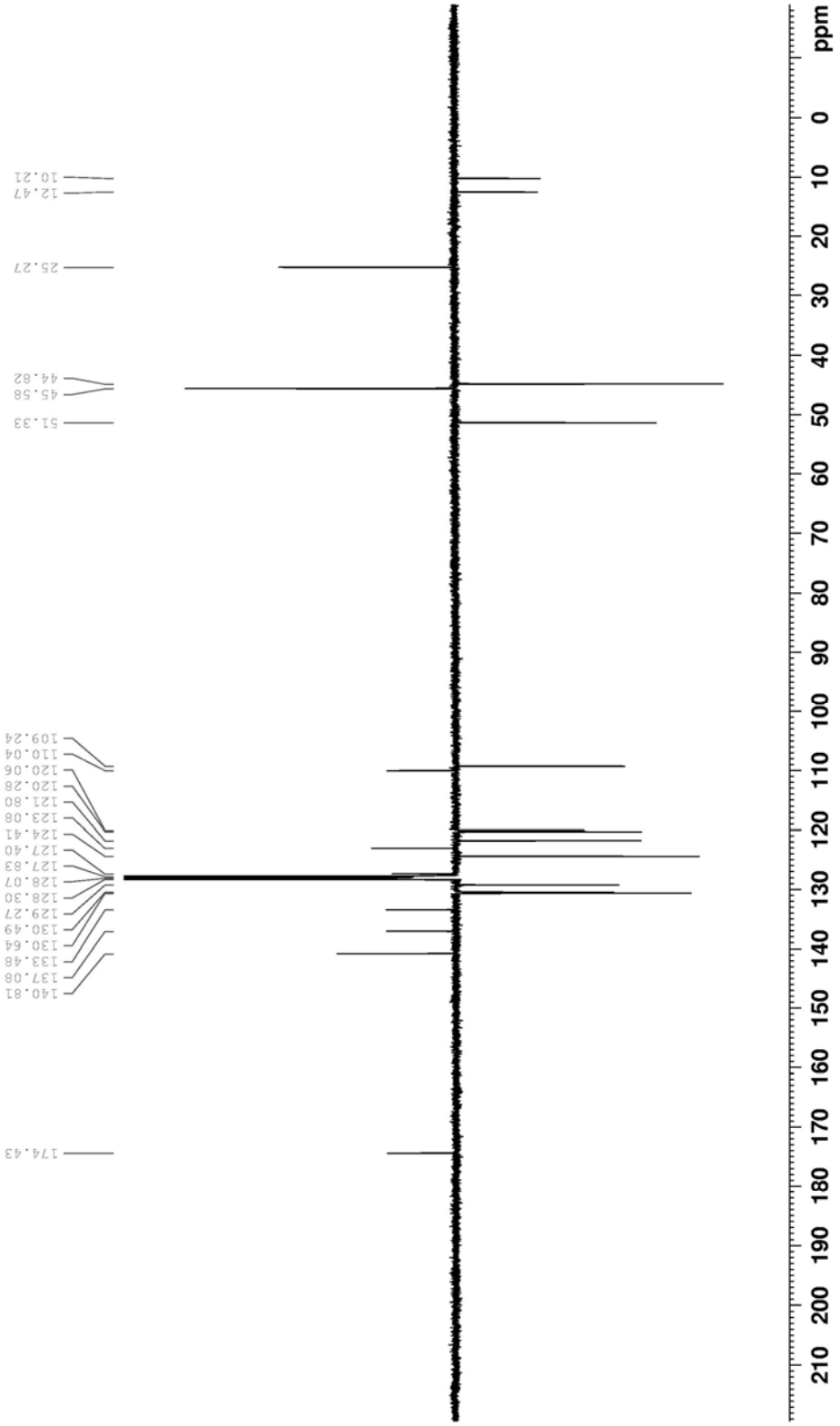
^{1}H NMR of G (400 MHz, C_6D_6)



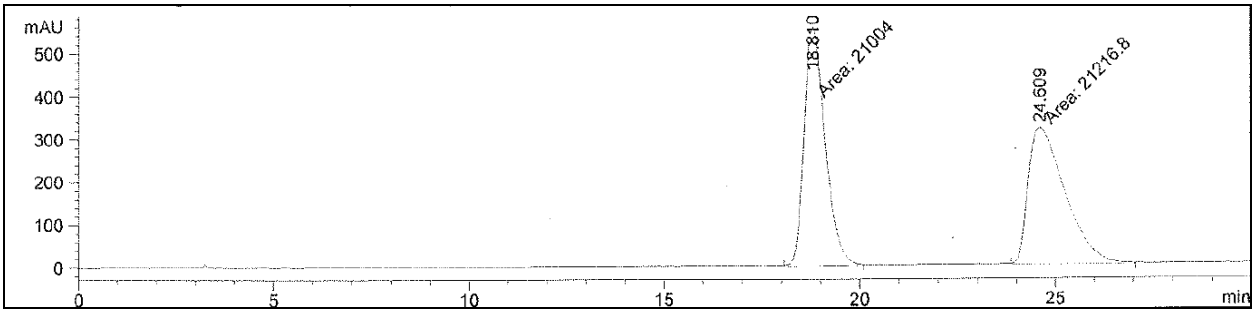


^{13}C NMR spectrum of G (100 MHz, C_6D_6)

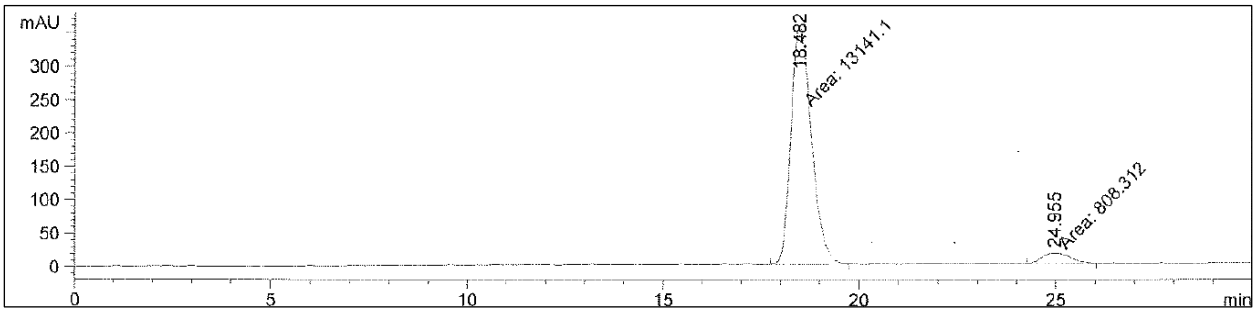




HPLC resolution of racemic **G** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



Enantiomeric excess of **G** (Chiracel OD column, 99:1 hexanes:isopropanol – 97.5:2.5 hexanes isopropanol over 30 min, 1 mL/min, 220 nm)



Signal 2: DAD1 B, Sig=220,4 Ref=450,80

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.482	MM	0.6136	1.31411e4	356.95868	94.2054
2	24.955	MM	0.8283	808.31226	16.26467	5.7946
Totals :				1.39495e4	373.22335	

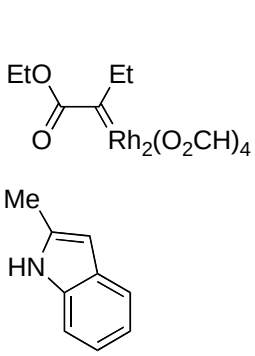
Computational Details

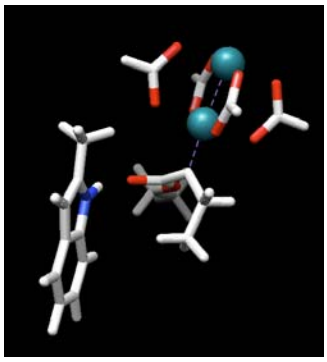
Cartesian coordinates and total energies of the optimized structures:

Full g09 reference:

Gaussian 09, Revision A.02,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,
G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian,
A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,
M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,
Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,
J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers,
K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand,
K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi,
M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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,
R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,
P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,
O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,
and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Cartesian coordinates of the optimized pre-reaction complex (B3LYP/gen [lanl2dz&6-311+G(d,p)])





Charge = 0 Multiplicity = 1

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C 1.033916,1.915944,-0.272513

O 0.621732,3.171333,-0.204607

C 1.109676,4.092146,-1.231751

C 0.980736,0.892099,2.056104

C 2.398595,1.405776,2.322548

Rh -1.312758,0.110556,0.265426

C 0.467766,5.4369,-0.971484

O -1.894659,1.600685,-1.075055

C -3.039257,1.51399,-1.618778

O -3.911794,0.629533,-1.459428

Rh -3.51144,-0.967288,-0.171183

O -4.261138,0.136123,1.438955

C -3.485244,0.893674,2.062651

O -2.251171,1.107585,1.843292

H 0.835411,3.681417,-2.204578

H 2.198475,4.130962,-1.165987

H 0.232038,1.464958,2.646234

H 0.822765,-0.133267,2.411581

H 2.627918,1.315785,3.386279

H 2.508944,2.456796,2.045162

H 3.139754,0.824033,1.77201

H -0.620178,5.366095,-1.024588

H 0.805316,6.151371,-1.726823

H 0.74522,5.82184,0.012033

H -3.283393,2.327187,-2.3163

H -3.907522,1.451776,2.909374

C 5.106635,-0.448159,-0.336061

C 5.640666,0.804813,-0.026629

C 6.885209,0.842088,0.592304

C 7.583317,-0.342678,0.893139

C 7.05164,-1.5868,0.580369

C 5.795801,-1.657557,-0.042649

N 3.913581,-0.791071,-0.939791

C 3.821743,-2.169636,-1.034507

C 4.955519,-2.728902,-0.498499

C 2.63427,-2.815853,-1.668766

H 5.107985,1.717456,-0.270348

H 7.328376,1.799716,0.842052

H 8.553321,-0.278547,1.373533

H 7.60064,-2.492959,0.813785

H 3.181321,-0.139073,-1.19128

H 5.164596,-3.786548,-0.443849

H 2.672939,-3.896434,-1.523932

H 2.605057,-2.620487,-2.746841

H 1.698409,-2.440437,-1.244609

O -0.9089,-1.476854,1.556106

C -1.786657,-2.386025,1.698287

O -2.910488,-2.467893,1.152932

H -1.509716,-3.193912,2.389027

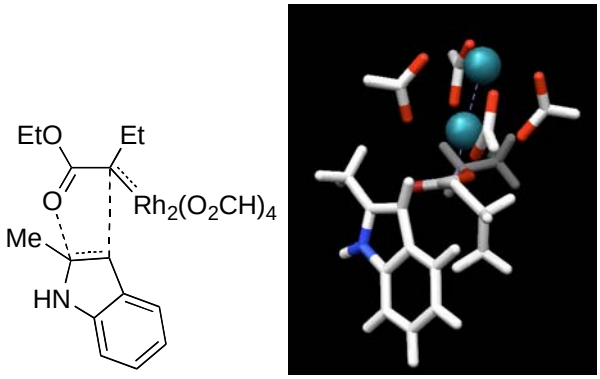
O -0.58966,-1.008324,-1.339032

C -1.383869,-1.774489,-1.967038

O -2.600214,-1.980582,-1.747818

H -0.932466,-2.321332,-2.805971

Cartesian coordinates of the optimized transition state (**D**) for the reaction between 2-methylindole and $Et(EtO_2C)C{=}Rh_2(O_2CH)_4$ shown in Fig. 1(b)



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C	-1.4507278179,0.3645431501,-0.4738207676
C	-2.1648596072,1.6669272194,-0.2562805657
O	-1.9624020064,2.4190195645,-1.3565717636
C	-2.3837166849,3.8058474178,-1.2837707111
C	-1.9158084687,-0.4366599175,-1.640123864
C	-3.3909224768,-0.3843732866,-2.0575762985
Rh	0.6167813627,0.3961521369,-0.170738224
C	-2.028024499,4.457367882,-2.6038818179
O	0.7000662369,2.4714910566,0.0824335824
C	1.8344029077,3.0216322915,0.2151823551
O	2.969692188,2.4876822723,0.2078585504
Rh	3.1114281097,0.41736582,-0.0389025433
O	3.1361560153,0.6645006859,-2.110590325
C	2.0407943202,0.7005422113,-2.7176900809
O	0.870846014,0.6140492835,-2.2349909571
H	-1.8690699282,4.2733892991,-0.442154138
H	-3.457779758,3.8343553739,-1.0863271493
H	-1.2963293725,-0.0074346494,-2.4475859342
H	-1.5512237908,-1.4617173349,-1.5489804319

H -3.5374440446,-0.9891371314,-2.9563225073

H -3.7001558718,0.636479556,-2.2912211518

H -4.0498695453,-0.7781596413,-1.2839044575

H -0.9530262356,4.4042639376,-2.7866338205

H -2.3245943136,5.5097541596,-2.5845088795

H -2.5450568378,3.9713850461,-3.4344398042

H 1.8098459612,4.1120886816,0.3550649487

H 2.0860304555,0.8221416022,-3.8091748102

C -4.3217627138,-1.7578808924,1.3085636402

C -5.4781102727,-2.4480339828,0.9650259857

C -5.3345737015,-3.5559555888,0.1302465252

C -4.0718820618,-3.9535888042,-0.3337944569

C -2.9228961696,-3.2422160196,0.0037708553

C -3.0432797359,-2.1149509576,0.8219985927

N -4.1390407188,-0.6656478626,2.1564333772

C -2.8238550778,-0.3243248163,2.2253361978

C -2.0996010959,-1.1487551876,1.3496087545

C -2.3423040112,0.6749693247,3.2169715565

H -6.4518772676,-2.1522664611,1.3392016146

H -6.2121155466,-4.1252492147,-0.1531574146

H -3.9917158224,-4.8314662818,-0.9646245022

H -1.9507680588,-3.5578490993,-0.356389415

H -4.8783268631,-0.1554060573,2.6146958523

H -1.0361875085,-1.2885318756,1.4210567814

H -1.3384806542,1.0017179181,2.9595666082

H -2.3144988892,0.2134936262,4.2118674059

H -2.9989030836,1.5454695894,3.2547367078

O 0.7393913767,-1.6788145727,-0.3800991245

C 1.8906991395,-2.2164924242,-0.3949475886

O 3.0089122491,-1.6629027284,-0.2901072706

H 1.892995276,-3.3093321166,-0.5154432905

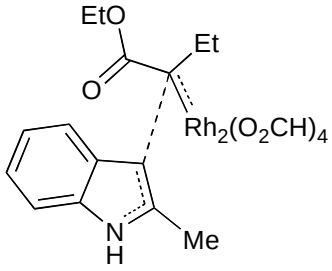
O 0.649082132,0.1828974267,1.9160683154

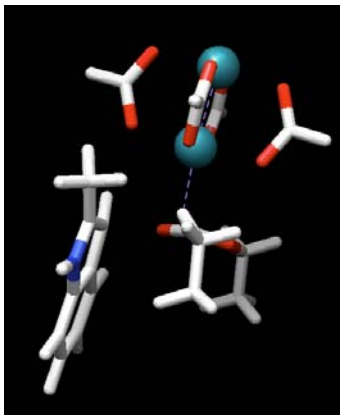
C 1.7661524593,0.1236885945,2.5177437638

O 2.9162688399,0.1764163095,2.0265515209

H 1.703223291,0.0115896789,3.6097697776

Another transition state (D*), which does not possess oxocarbenium character for the reaction between 2-methylindole and $Et(EtO_2C)C=Rh_2(O_2CH)_4$:





E+ZPVE= -1764.057585 a.u. Im. Freq,ν_i=128.7i cm^{-1}

C 2.8386494867,3.083775627,3.0901562796

C 1.9968734608,3.8211310199,3.9378090645

O 2.0379347154,0.2893013806,0.0339617807

N -0.8224956905,1.3958255282,3.9199835821

C -0.7733695089,0.2197453933,3.2333265418

C 0.3447601779,2.1301094085,3.724114905

C 1.1578388145,1.3816842952,2.8420979381

C -0.3917108392,0.2346318728,0.1460218273

C 0.9562111993,0.5665588183,-0.4220975615

O 0.7664699752,1.1456505114,-1.629611622

C 1.9263801766,1.2710664924,-2.4952540797

C -1.456151137,1.2730146145,0.141217131

C -1.1085277281,2.7394843325,0.4226533182

Rh -0.9837797637,-1.6890251291,-0.3958592384

C 2.5925105431,2.6263679011,-2.3286360304

C 0.412653591,0.1808601741,2.4873503997

C 0.7304935606,3.3497985871,4.271102167

C 2.4350103124,1.8714103517,2.5392159923

H 1.5236959404,1.1431802369,-3.5005087454

H 2.613580001,0.4553529017,-2.2721743192

H -1.8217707613,1.1805674825,-0.8981352323

H -2.2991765654,0.9322544549,0.7472920647

H -2.0023005128,3.3566607155,0.2948280767

H -0.347773271,3.1076079217,-0.2670785417

H -0.7430326896,2.883377879,1.4389478523

H 1.8869220417,3.4369253048,-2.5265835589

H 3.4207156481,2.7156992748,-3.0380814176

H 2.9925285209,2.7441694137,-1.3200530635

H 0.8281749957,-0.728550978,2.0846425264

O 0.8112430993,-2.0649398297,-1.3939516445

C 0.9564356177,-3.1576262034,-2.0184508443

O 0.1380733726,-4.1003050137,-2.1433451262

H 1.9306535186,-3.2857804565,-2.5110400379

Rh -1.7402084731,-3.9106201265,-1.2544289377

O -2.434872506,-2.9138315774,-2.9523909946

C -2.3045425571,-1.668911625,-3.0102794747

O -1.7769593687,-0.8920262314,-2.1577823723

H -2.6935874057,-1.1741637239,-3.9113889037

O -2.8861321519,-1.5128550935,0.4752410947

C -3.7212555307,-2.4552147585,0.3107969229

O -3.566203323,-3.5346207726,-0.304454146

H -4.7050267138,-2.2940477737,0.7754712514

O -0.2676269683,-2.7232549665,1.2771986387

C -0.4113587609,-3.9840289662,1.3323353132

O -0.9732000578,-4.7375611611,0.5056413622

H 0.0100680658,-4.4629592938,2.2277518345

H 3.0864928569,1.3146402118,1.8805952633

H 3.8261894125,3.4685748094,2.8620270975

H 2.3400838705,4.7640494794,4.3474446893

H 0.0816710745,3.9049997838,4.9394884567

C -1.8608948547,-0.784184481,3.3852333969

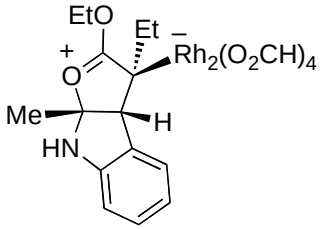
H -2.6749103309,-0.5986185009,2.6791611175

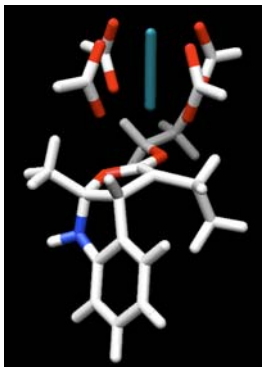
H -1.4786379194,-1.7796127304,3.1698244787

H -2.2661462235,-0.7637930971,4.400995106

H -1.586467917,1.6717981313,4.5174828516

Cartesian coordinates of optimized structure of ylide (**E**) for the reaction between 2-methylindole and $Et(EtO_2C)C{=}Rh_2(O_2CH)_4$ shown in Fig. 1(c)





E+ZPVE= -1764.100099 a.u.

O -1.9632097101,1.6134372422,1.2279263099

C -1.482849425,0.2719964541,-0.6008297544

C -1.4924157701,1.5341690406,-0.0024886249

O -1.0968778011,2.6410459868,-0.5787589628

C -0.9730451155,3.8545592593,0.2220846426

C -1.5521085366,0.1358093554,-2.1155292285

C -2.7806854422,0.7970264409,-2.7687284543

Rh 0.8564960226,-0.1281889394,-0.1402207235

C -0.4569323801,4.9406785924,-0.6960707531

O 1.100316766,1.323895947,1.3552696845

C 2.2416471535,1.4553431488,1.8903851328

O 3.2943955556,0.8205512644,1.640913868

Rh 3.2545520951,-0.6528178686,0.1618719362

O 3.6583952804,0.7933205846,-1.2829284731

C 2.6923874824,1.3935066942,-1.8182498215

O 1.4569741662,1.2556505735,-1.5831691908

H -0.285441329,3.6426484632,1.0412460677

H -1.9547388723,4.0963845807,0.6339949694

H -0.6517600224,0.5736496337,-2.5488870859

H -1.5149548394,-0.9255079039,-2.3677830432

H -2.760467435,0.631148209,-3.850346852

H -2.777766407,1.8771960452,-2.6015821164

H -3.7201223055,0.3945113165,-2.3868065214

H 0.5137401423,4.6671319627,-1.11331448

H -0.3430285202,5.8692692668,-0.1304576084

H -1.1516971979,5.1224540514,-1.5187301001

H 2.312080326,2.2245243416,2.6729901597

H 2.9477682958,2.1342045645,-2.5890737677

C -4.6133165636,-0.4308918364,0.7254508345

C -5.9738510652,-0.6768949075,0.5709876513

C -6.3661198681,-1.6152466072,-0.3878222067

C -5.4228617054,-2.2892207849,-1.1629492187

C -4.0578182661,-2.0271124089,-0.9942656974

C -3.6571784522,-1.0855446767,-0.0588944566

N -3.9959734591,0.4434821246,1.6321568973

C -2.5674179909,0.2904322664,1.598920063

C -2.2708582104,-0.6371837401,0.3640325406

C -1.9614240258,-0.0810777178,2.9370033716

H -6.7102243525,-0.1613897408,1.177553418

H -7.4214488359,-1.8243081442,-0.5228958134

H -5.7462423112,-3.021521835,-1.8930887885

H -3.3236009033,-2.5615360258,-1.5868006617

H -4.4308452015,0.6065062151,2.5284505088

H -1.6690493049,-1.4952636859,0.664770089

H -0.8761327238,-0.1151630107,2.8680868908

H -2.3271824034,-1.0647500011,3.2408752299

H -2.247617982,0.6537567759,3.6953869544

O 0.8337765655,-1.6406724676,-1.5842397479

C 1.9091990346,-2.2534051936,-1.8448902743

O 3.0451367757,-2.086813151,-1.331577859

H 1.8361182047,-3.0301354029,-2.6189792283

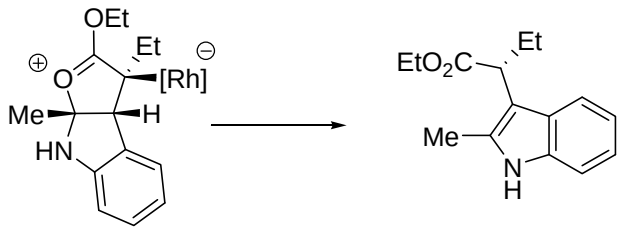
O 0.4851330478,-1.5870973298,1.3261732336

C 1.4650553912,-2.2140302226,1.829608045

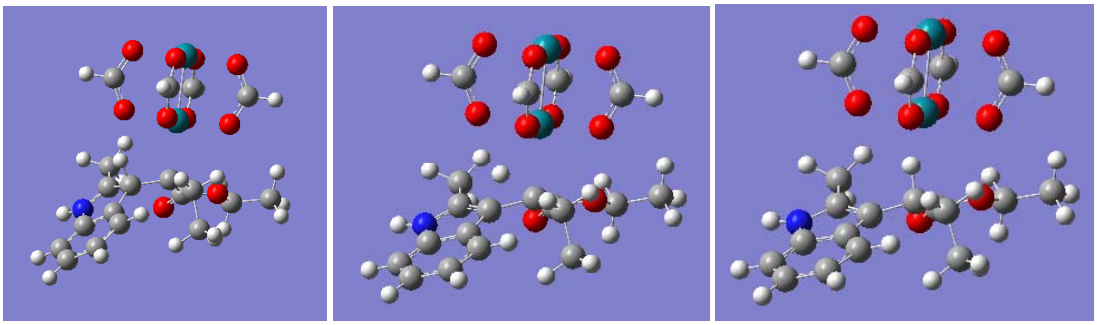
O 2.6869770373,-2.0680577058,1.5844755529

H 1.206180392,-2.9789920933,2.5752664633

Calculations on the stepwise conversion of **E** to **F**. These computations suggest that an intramolecular 1,2-hydride shift for the conversion of **E** to **F** is not plausible ($\Delta E(ZPE)^{\ddagger}$ = 30.2 kcal/mol) at –78 °C.



E **F**



IRCreverse (Reactant) TS IRCforward (ending point)

Reaction barrier (kcal/mol):

$\Delta E^{\neq}$=34.3; $\Delta(E+ZPVE)^{\neq}$=30.2; $\Delta H^{\neq}$=30.7; $\Delta G^{\neq}$=29.1

This reactant complex is 25.7 kcal/mol lower in energy than isolated carbene, indole and Rh-catalyst. The TS itself is higher in energy by 8.7 kcal/mol with respect to isolated reactants

Reactant

File: 1SModIndProd_Gen.log

E=-1764.5149405 a.u.

Zero-point correction= 0.414842 (Hartree/Particle)

Thermal correction to Energy= 0.447697

Thermal correction to Enthalpy= 0.448641

Thermal correction to Gibbs Free Energy= 0.352047

Sum of electronic and zero-point Energies= -1764.100099

Sum of electronic and thermal Energies= -1764.067243

Sum of electronic and thermal Enthalpies= -1764.066299

Sum of electronic and thermal Free Energies= -1764.162894

O,0,-1.9632097101,1.6134372422,1.2279263099

C,0,-1.482849425,0.2719964541,-0.6008297544

C,0,-1.4924157701,1.5341690406,-0.0024886249

O,0,-1.0968778011,2.6410459868,-0.5787589628

C,0,-0.9730451155,3.8545592593,0.2220846426

C,0,-1.5521085366,0.1358093554,-2.1155292285

C,0,-2.7806854422,0.7970264409,-2.7687284543

Rh,0,0.8564960226,-0.1281889394,-0.1402207235

C,0,-0.4569323801,4.9406785924,-0.6960707531

O,0,1.100316766,1.323895947,1.3552696845

C,0,2.2416471535,1.4553431488,1.8903851328

O,0,3.2943955556,0.8205512644,1.640913868

Rh,0,3.2545520951,-0.6528178686,0.1618719362

O,0,3.6583952804,0.7933205846,-1.2829284731

C,0,2.6923874824,1.3935066942,-1.8182498215

O,0,1.4569741662,1.2556505735,-1.5831691908

H,0,-0.285441329,3.6426484632,1.0412460677

H,0,-1.9547388723,4.0963845807,0.6339949694

H,0,-0.6517600224,0.5736496337,-2.5488870859

H,0,-1.5149548394,-0.9255079039,-2.3677830432

H,0,-2.760467435,0.631148209,-3.850346852

H,0,-2.777766407,1.8771960452,-2.6015821164

H,0,-3.7201223055,0.3945113165,-2.3868065214

H,0,0.5137401423,4.6671319627,-1.11331448

H,0,-0.3430285202,5.8692692668,-0.1304576084

H,0,-1.1516971979,5.1224540514,-1.5187301001

H,0,2.312080326,2.2245243416,2.6729901597

H,0,2.9477682958,2.1342045645,-2.5890737677

C,0,-4.6133165636,-0.4308918364,0.7254508345

C,0,-5.9738510652,-0.6768949075,0.5709876513

C,0,-6.3661198681,-1.6152466072,-0.3878222067

C,0,-5.4228617054,-2.2892207849,-1.1629492187

C,0,-4.0578182661,-2.0271124089,-0.9942656974

C,0,-3.6571784522,-1.0855446767,-0.0588944566

N,0,-3.9959734591,0.4434821246,1.6321568973

C,0,-2.5674179909,0.2904322664,1.598920063

C,0,-2.2708582104,-0.6371837401,0.3640325406

C,0,-1.9614240258,-0.0810777178,2.9370033716

H,0,-6.7102243525,-0.1613897408,1.177553418

H,0,-7.4214488359,-1.8243081442,-0.5228958134

H,0,-5.7462423112,-3.021521835,-1.8930887885

H,0,-3.3236009033,-2.5615360258,-1.5868006617

H,0,-4.4308452015,0.6065062151,2.5284505088

H,0,-1.6690493049,-1.4952636859,0.664770089

H,0,-0.8761327238,-0.1151630107,2.8680868908

H,0,-2.3271824034,-1.0647500011,3.2408752299

H,0,-2.247617982,0.6537567759,3.6953869544

O,0,0.8337765655,-1.6406724676,-1.5842397479

C,0,1.9091990346,-2.2534051936,-1.8448902743

O,0,3.0451367757,-2.086813151,-1.331577859

H,0,1.8361182047,-3.0301354029,-2.6189792283

O,0,0.4851330478,-1.5870973298,1.3261732336

C,0,1.4650553912,-2.2140302226,1.829608045

O,0,2.6869770373,-2.0680577058,1.5844755529

H,0,1.206180392,-2.9789920933,2.5752664633

TS E= -1764.4602321 a.u. Im. Freq=1261.3346i cm^{-1}

File: 1SIndHmigTS_Gen.log

Zero-point correction= 0.408258 (Hartree/Particle)

Thermal correction to Energy= 0.441852

Thermal correction to Enthalpy= 0.442797

Thermal correction to Gibbs Free Energy= 0.343763

Sum of electronic and zero-point Energies= -1764.051974

Sum of electronic and thermal Energies= -1764.018380

Sum of electronic and thermal Enthalpies= -1764.017435

Sum of electronic and thermal Free Energies= -1764.116469

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C,0,-1.4304563345,1.0598197515,-0.2810432747

C,0,-1.2286722063,2.3353403898,0.4779471498

O,0,-0.3798261584,3.1594797054,-0.162270857

C,0,-0.0956159933,4.4180989228,0.4894797645

C,0,-1.5259909467,1.2368442917,-1.7955527957

C,0,-2.6623393769,2.1731814838,-2.2457707315

Rh,0,0.7335208399,-0.0928675238,-0.0914125142

C,0,0.861500341,5.1875614438,-0.3980430772

O,0,1.4018616291,1.1089595942,1.4845935991

C,0,2.5784742875,0.9327601006,1.9205283866

O,0,3.4365000954,0.1013108387,1.5337320046

Rh,0,2.9455873645,-1.2062629824,-0.0211532062

O,0,3.6119786109,0.1941157766,-1.4026393527

C,0,2.7969376137,1.0593297372,-1.8125820222

O,0,1.5863280196,1.2130898343,-1.4840155128

H,0,0.3352053298,4.2086079793,1.4711800733

H,0,-1.033869654,4.9568965609,0.6435731401

H,0,-0.5787013731,1.6479697387,-2.1404890616

H,0,-1.6087557162,0.257351703,-2.2667594626

H,0,-2.7172081194,2.1970419945,-3.3385877729

H,0,-2.4778498418,3.1950348116,-1.9058138176

H,0,-3.6399724046,1.8671812222,-1.8680524671

H,0,1.791067735,4.6334241903,-0.5421105793

H,0,1.0997551959,6.1488410649,0.0657261555

H,0,0.4192061488,5.3802120098,-1.378197818

H,0,2.8805907521,1.5955026649,2.7438568158

H,0,3.1814604008,1.7766015236,-2.5512638186

C,0,-4.4105440424,-1.1240058693,0.7586256561

C,0,-5.5591945009,-1.8826962384,0.5528218078

C,0,-5.9504675804,-2.1030601898,-0.7610281994

C,0,-5.199368907,-1.5777481185,-1.8221447507

C,0,-4.0532520319,-0.822508706,-1.5992083318

C,0,-3.6375428536,-0.5709879348,-0.2839342327

N,0,-3.7956279607,-0.7909180904,1.9592032144

C,0,-2.6671191805,-0.0714350321,1.7617288056

C,0,-2.5040217943,0.1306430805,0.3588621215

C,0,-1.8189678523,0.2781796887,2.9345995498

H,0,-6.1224476229,-2.2888382605,1.3855029894

H,0,-6.8384111314,-2.6889909004,-0.9666309062

H,0,-5.5160697021,-1.7658882522,-2.8413825361

H,0,-3.4988962646,-0.4479441365,-2.4456324632

H,0,-4.0863333402,-1.1268557878,2.8648991723

H,0,-1.354792508,-0.3053647719,0.1706774161

H,0,-0.7904292227,0.4657706329,2.6400778303

H,0,-1.8330531718,-0.5420499147,3.6588968773

H,0,-2.1917364348,1.1888737261,3.4086761529

O,0,0.2375303832,-1.4025404535,-1.6436174597

C,0,1.102544086,-2.2473710068,-2.022380967

O,0,2.2661017224,-2.4197931437,-1.5830196829

H,0,0.7870128765,-2.9099821961,-2.8404264596

O,0,0.1064258675,-1.5460394568,1.298935267

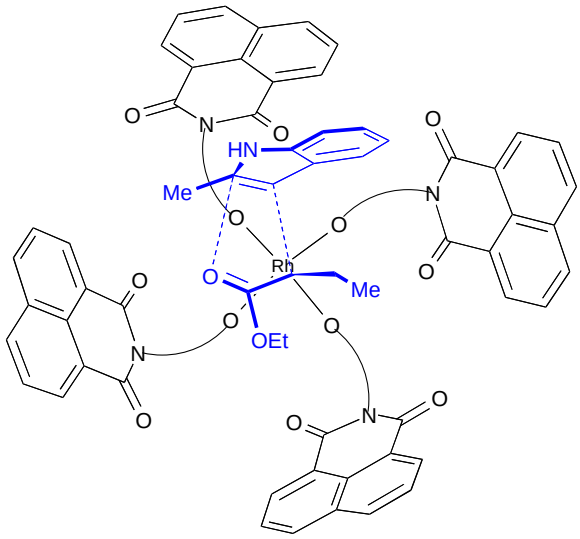
C,0,0.9347993463,-2.4263148106,1.6843968083

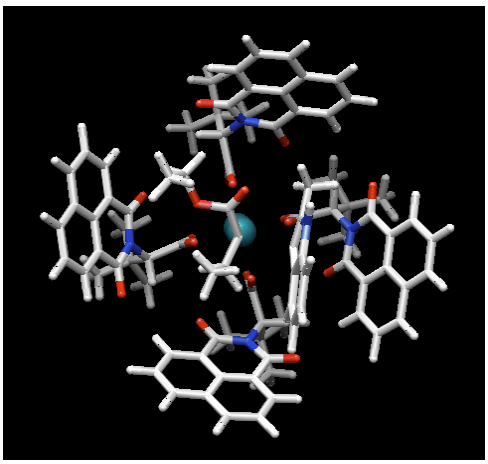
O,0,2.1367279446,-2.5544168975,1.3574977478

H,0,0.5395898439,-3.1634012447,2.3978943298

Cartesian coordinates of the optimized transition state for the reaction between 2-methylindole and Et(EtO$_2$C)C=Rh$_2$ Rh$_2$(*S*-NTTL)$_4$ shown in Fig. 2(b)

In this case atoms C, O, N, H where treated at smaller basis set, 6-31G(d).





E+ZPVE -5210.852522 a.u. Im. Freq,ν_i=150.6i cm^{-1}

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Rh -0.3242714622,0.3219545075,-3.0328448264

C -0.6960398836,2.8296687312,-1.5918199282

C -1.0170158719,4.3278704277,-1.4048357954

C -1.2004019622,5.2165599287,-2.684941436

C 0.0147754747,5.2314671366,-3.6329121637

C -1.4958654052,6.6666479716,-2.2402317056

C -2.44232953,4.698022408,-3.4466283755

C -0.7096283667,5.5328965576,0.7260354044

C 0.1919172218,6.1694906045,1.7186686959

C -0.3531718779,6.885066271,2.7710622175

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C 1.8574557541,7.3897383074,3.6237995775

C 2.4516642185,6.6576580682,2.5626459468

C 1.5971878436,6.045962304,1.59516023

C 2.1570250352,5.3042616521,0.5258969805

C 3.5306432465,5.1576741786,0.4272864828

C 4.3803844849,5.7584842137,1.3811220465

C 3.8557238242,6.4966376596,2.4225186921

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C 4.5220208288,1.2541189679,-3.4267316651

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C 6.0170424551,1.5910429739,-3.2265384249

C 3.8668958627,2.4599396998,-4.1406936479

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C 7.1092036853,0.618993896,1.6635542515

C 7.8596074953,-0.174465216,2.555478632

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C 5.1208686189,-1.9816301774,-0.1074274283

C 4.9212630477,-3.3518224252,-0.0749292133

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C 6.5600590652,-3.5861109436,1.6966235325

C 4.3713886638,-1.1543700451,-1.0828419318

C 0.2781438937,-2.3512203055,-2.0288541291

C 0.7186354262,-3.8263999206,-2.1153483258

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C 1.6894884242,-3.8688852815,-4.4411484574

C 1.0850737199,-6.0177441561,-3.3281164818

C -0.7313798793,-4.5190723306,-4.1838695084

C -1.2776237689,-4.44806012,-0.7667764917

C -1.8560751369,-5.1745011908,0.3896884513

C -3.2085567459,-5.0572690948,0.6640378747

C -3.7757079336,-5.7664180042,1.7452354166

C -2.9964781189,-6.585243088,2.5366213945

C -1.6032650964,-6.716625585,2.2931653468

C -1.0319322521,-5.9890811579,1.2050126326

C 0.3599966862,-6.0714438085,0.9571156986

C 1.1633915135,-6.8675914711,1.7568998788

C 0.6024823313,-7.6039377945,2.8212847549

C -0.7511489968,-7.5283294319,3.0861771212

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C -2.8202698709,-0.3855872208,-1.755236228

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C -5.8354656697,1.5577743817,0.6982899745

C -6.018288823,2.927327183,0.7871495693

C -6.7754792498,3.4773039508,1.844029707

C -7.3375040139,2.6586307967,2.8031188591

C -7.170418558,1.2497036698,2.7438602751

C -6.4098952568,0.6996675507,1.6669141581

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C -7.5285126368,-1.0008746151,3.5998319655

C -7.7217675084,0.3620157405,3.7050145419

C -5.463946033,-1.2899895358,0.4443103606

N -0.1065088464,4.9063232956,-0.3807819376

N 4.5992763428,0.2356197217,-1.0663454712

N 0.1048720595,-4.5867190658,-0.9952207448

N -4.969575663,-0.4039509672,-0.5266106002

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O 1.7230959662,3.995837263,-1.4052324436

O 1.8633640562,0.5626223628,-0.8012803344

O 1.7073263728,0.7050762562,-3.0556619881

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O 0.2527172929,-1.8748385689,-0.8438666091

O 0.072704112,-1.7205651593,-3.1000669301

O -1.9602066561,-3.7542636031,-1.5083349158

O 2.1894075814,-5.2793247587,-0.3195938663

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O -4.4524605382,1.7119372582,-1.2216215181

O -5.2950107337,-2.5018041991,0.3524985214

H -1.987082704,4.3270340374,-0.9006115435

H -0.2322080497,5.8270772449,-4.520996633

H 0.2838171613,4.2239639698,-3.9537166178

H 0.8932013602,5.6844994187,-3.1640650238

H -1.7163012588,7.2792593094,-3.1221012154

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H -2.3572704009,6.7194413411,-1.5658984779

H -2.6596268624,5.3656549127,-4.2890566236

H -3.3280405358,4.6791948853,-2.7990355942

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H -1.4328474613,6.961820403,2.8426559261

H 0.0426888401,8.062868202,4.5415582634

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H 5.4544744519,5.6297250392,1.2881624416

H 4.5128312533,6.9601192027,3.154616002

H 3.880578843,2.0829277322,-1.5525562021

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H 3.3820583357,-0.2864527118,-4.4890826324

H 6.5670796372,0.7631686179,-2.764670151

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H -7.9170384944,3.084833165,3.6184074432

H -6.6297774121,-2.6066116084,2.4343951042

H -7.9554993929,-1.669541681,4.3415327674

H -8.3007513633,0.7730845295,4.5284248313

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O -2.027860463,1.3109943792,2.0930021069

C -2.5979107978,2.5403091428,2.6115206482

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C -1.2814538988,-1.5431685002,3.4402773752

C -3.103432436,2.3544614284,4.0342393613

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