Supporting Information

The Chiral Crown Conformation of Rh_2(*S*-PTTL)$_4$: Enantioselective Cyclopropanation with α-Alkyl-α-diazoesters

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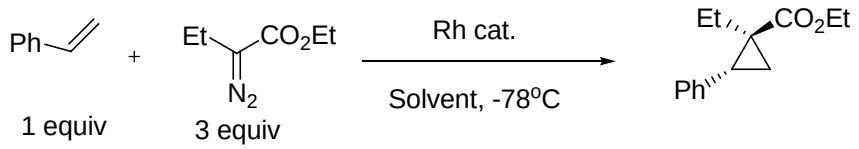
Experimental Procedures

General Considerations

All non-aqueous reactions were carried out in glassware that was flame-dried under vacuum and cooled under nitrogen. CH_2Cl_2, toluene, diethyl ether, and hexanes were dried with columns packed with activated neutral alumina. THF was distilled from sodium/benzophenone. Chromatography was performed on silica gel (silicycle 40-63D, 60Å). For ^{13}C NMR, multiplicities were distinguished using a 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 mesitylene 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, and ethyl 2-diazo-5-methylhexanoate were prepared from the corresponding β-ketoesters according to literature protocol.[1] (*E*)-1-phenylbutadiene was prepared according to a literature procedure.[2] Dirhodium tetrakis triphenylacetate,[3] dirhodium tetrakis *N*-phthaloyl (*S*)-valinate, and dirhodium tetrakis *N*-phthaloyl (*S*)-*tert*-leucinate were also prepared according to methods described in the literature.[4] The "racemic" (+/–) $Rh_2(PTV)_4$ was prepared by mixing an equimolar amount of each enantiomer, and then dissolving the mixture in CH_2Cl_2 and subsequently evaporating the solvent. X-ray quality crystals of Rh_2(*S*-PTTL)$_4$ were grown by slow evaporation of 20:2:1 drop hexanes/toluene/ethyl acetate. Enantiomeric excesses were measured on materials directly after chromatography (i.e. the reported ee's have not been enhanced through crystallization).

Optimization Table

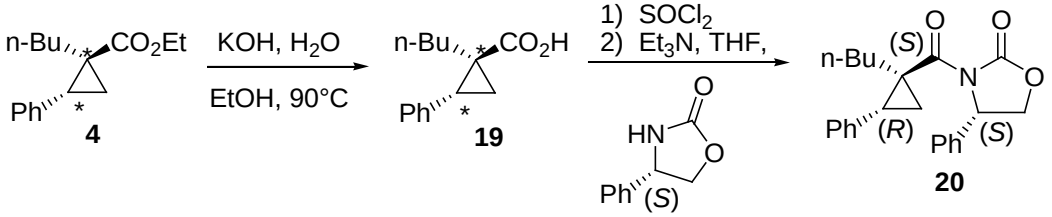


Entry	Rh cat.	Solvent	Yield	dr	ee
1	Rh_2(*S*-DOSP)$_4$	CH_2Cl_2	26%	84:16	0%
2	Rh_2(*R*-PTAD)$_4$	CH_2Cl_2	51%	82:18	-30%
3	Rh_2(*R*-PTAD)$_4$	PhMe	98%	90:10	-70%
4	Rh_2(*S*-PTPA)$_4$	PhMe	24%	>99:1	28%
5	Rh_2(*S*-PTV)$_4$	PhMe	95%	85:15	73%
6	Rh_2(*S*-PTTL)$_4$	CH_2Cl_2	94%	80:20	50%
7	**Rh_2(*S*-PTTL)$_4$**	**Hexanes**	**95%**	**92:8**	**79%**
8	Rh_2(S-PTTL)$_4$	Et_2O	92%	89:11	75%
9	Rh_2(S-PTTL)$_4$	PhMe	99%	90:10	72%

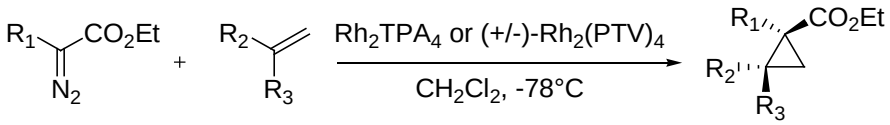
*Bold face denotes optimized conditions

Assignment of absolute configuration

For the cyclopropanations catalyzed by Rh_2(*S*-PTTL)$_4$ the absolute configuration was determined by x-ray diffraction of compound **20**, which was prepared from compound **19** (96% ee) and (*S*)-(+)-4-phenyl 2-oxazolidinone. From the x-ray data, it was determined that the absolute configuration of the cyclopropane is 1*S*, 2*R*.



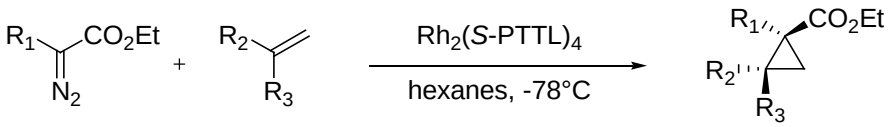
General procedure for cyclopropanation to provide racemic samples



In a dry round bottomed flask, Rh_2TPA_4 (3 mg, 0.002 mmol) or +/- $Rh_2(PTV)_4$ (2 mg, 0.002 mmol) and 0.40 mmol of alkene were dissolved in anhydrous CH_2Cl_2 (2.0 mL) and cooled by a bath of dry ice/acetone (−78 °C) under a nitrogen atmosphere. The appropriate diazoester (1.20 mmol) was dissolved in anhydrous CH_2Cl_2 (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 room temperature. The solvent was subsequently removed and the residue was chromatographed on silica gel.

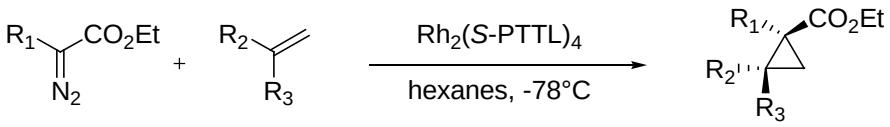
NOTE: Compounds **2**, **4**, **7**, and **10** were prepared according to previously described protocols.[5]

General procedure I for enantioselective cyclopropanation using Rh_2(*S*-PTTL)$_4$



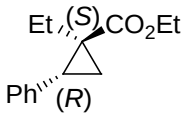
In a dry round bottomed flask, Rh_2(*S*-PTTL)$_4$ (2 mg, 0.002 mmol) and 0.44 mmol of alkene were dissolved in anhydrous hexanes (2.2 mL) and cooled by a bath of dry ice/acetone (−78 °C) under a nitrogen atmosphere. The appropriate diazoester (0.40 mmol) was dissolved in anhydrous hexanes (1.0 mL) and 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 room temperature. The solvent was subsequently removed and the residue was chromatographed on silica gel.

General procedure II for enantioselective cyclopropanation using Rh_2(*S*-PTTL)$_4$



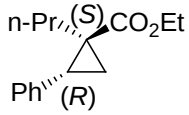
In a dry round bottomed flask, Rh_2(*S*-PTTL)$_4$ (2 mg, 0.002 mmol) and 0.40 mmol of alkene were dissolved in anhydrous hexanes (2.0 mL) and cooled by a bath of dry ice/acetone (−78 °C) under a nitrogen atmosphere. The appropriate diazoester (1.20 mmol) was dissolved in anhydrous hexanes (1.2 mL) and 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 room temperature. The solvent was subsequently removed and the residue was chromatographed on silica gel.

(1*S*,2*R*)-(+)-Ethyl 1-ethyl-2-phenylcyclopropane-1-carboxylate (2)



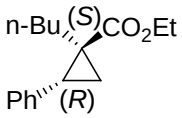
General procedure I was followed with 55 mg (0.39 mmol) of ethyl 2-diazobutanoate and 45 mg (0.43 mmol) of styrene to give 66 mg (0.30 mmol, 77%) of known compound **2** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be 92:8 by GC analysis. The enantiomeric excess of the major diastereomer was measured to be 79% ee by HPLC analysis (CHIRACEL OD column, 0.1% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 57 mg (0.40 mmol) of ethyl 2-diazobutanoate and 46 mg (0.44 mmol) of styrene gave 66 mg (0.30 mmol, 75%) of **2**. The diastereomer ratio was measured to be 92:8 by GC analysis. The enantiomeric excess of the major diastereomer was measured to be 79% ee by HPLC analysis. Alternatively, general procedure II with 40 mg (0.38 mmol) of styrene (99% purity) and 160 mg (1.13 mmol) of ethyl 2-diazobutanoate gave 76 mg (0.35 mmol, 92%) of **2**. A repetition of that experiment gave **2** in 98% yield. $[\alpha]^{20}_{D}$ = +78° (*c*. 1.04 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

(1*S*,2*R*)-(+)-Ethyl 2-phenyl-1-propylcyclopropane-1-carboxylate (3)



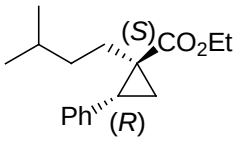
General procedure I was followed with 62 mg (0.40 mmol) of ethyl 2-diazopentanoate and 45 mg (0.44 mmol) of styrene to give 77 mg (0.33 mmol, 83%) of **3** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. Two peaks were detected in a 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 94% ee by HPLC analysis (CHIRACEL OD column, 0.2% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 67 mg (0.43mmol) of ethyl 2-diazopentanoate and 49 mg (0.47 mmol) of styrene gave 85 mg (0.37 mmol, 86%) of **3**. Two peaks were detected in a > 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 94% ee by HPLC analysis. Alternatively, general procedure II with 23 mg (0.22 mmol) of styrene (99% purity) and 104 mg (0.67 mmol) of ethyl 2-diazopentanoate gave 52 mg (0.22 mmol, 100%) of **3**. A repetition of that experiment gave **3** in 100% yield. $[\alpha]^{20}_D$ = +83° (*c*. 1.95 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.33-7.27 (m, 2H), 7.26-7.18 (m, 3H), 4.25-4.12 (m, 2H), 2.75 (dd, *J* = 9.0 Hz, 7.1 Hz, 1H), 1.69 (m, 1H), 1.67-1.58 (m, 1H), 1.43-1.27 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.19 (dd, *J* = 7.2 Hz, 4.6 Hz, 1H), 0.83-0.78 (m, 1H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 175.0 (u), 137.2 (u), 129.3 (dn), 128.1 (dn), 126.6 (dn), 60.6 (u), 32.1 (dn), 30.7 (u), 30.5 (u), 20.7 (u), 17.9 (u), 14.3 (dn, 2 carbons); IR ($CHCl_3$, cm^{-1}): 3020, 2962, 1709, 1458, 1382, 1295, 1217, 1158, 757, 699, 669; HRMS-ESI m/z: [M+], calcd for $C_{15}H_{20}O_2$, 232.1463; found 232.1454.

(1*S*,2*R*)-(+)-Ethyl 1-butyl-2-phenylcyclopropane-1-carboxylate (4)



General procedure I was followed with 73 mg (0.43 mmol) of ethyl 2-diazohexanoate and 49 mg (0.47 mmol) of styrene to give 92 mg (0.37 mmol, 86%) of **4** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. Two peaks were detected in a 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 96% ee by HPLC analysis (CHIRACEL OD column, 0.1% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 75 mg (0.44 mmol) of ethyl 2-diazohexanoate and 51 mg (0.49 mmol) of styrene gave 88 mg (0.36 mmol, 82%) of **4**. Two peaks were detected in a > 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 97% ee by HPLC analysis. Alternatively, general procedure II with 20 mg (0.19 mmol) of styrene (99% purity) and 97 mg (0.57 mmol) of ethyl 2-diazohexanoate gave 45 mg (0.18 mmol, 95%) of **4**. A repetition of that experiment gave **4** in 92% yield. $[\alpha]^{20}_{D}$ = +67° (*c*. 0.93 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

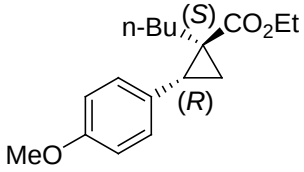
(1*S*,2*R*)-(+)-Ethyl 1-isopentyl-2-phenylcyclopropane-1-carboxylate (5)



General procedure I was followed with 81 mg (0.44 mmol) of ethyl 2-diazo-5-methylhexanoate and 51 mg (0.49 mmol) of styrene to give 102 mg (0.39 mmol, 89%) of **5** as a colorless oil. The

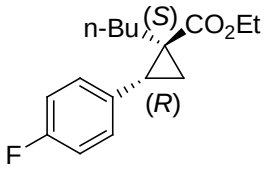
purity was measured to be ≥ 95% by ^{1}H NMR and GC. Two peaks were detected in a 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 99% ee by HPLC analysis (CHIRACEL OD column, 0.2% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 79 mg (0.43 mmol) of ethyl 2-diazo-5-methylhexanoate and 49 mg (0.47 mmol) of styrene gave 100 mg (0.38 mmol, 88%) of **5**. Two peaks were detected in a > 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 99% ee by HPLC analysis. Alternatively, general procedure II with 36 mg (0.34 mmol) of styrene (99% purity) and 176 mg (1.04 mmol) of ethyl 2-diazo-5-methylhexanoate gave 81 mg (0.31 mmol, 91%) of **5**. A repetition of that experiment gave **5** in 93% yield. $[\alpha]^{20}_D$ = +77° (*c*. 1.84 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.33-7.26 (m, 2H), 7.25-7.17 (m, 3H), 4.23-4.12 (m, 2H), 2.69 (dd, *J* = 9.4 Hz, 7.4 Hz, 1H), 1.64 (m, 1H), 1.59-1.51 (m, 1H), 1.30-1.22 (m, 1H), 1.28 (t, *J* = 7.3 Hz, 3H), 1.21-1.15 (m, 3H), 0.96-0.88 (m, 1H), 0.72 (d, *J* = 6.5 Hz, 3H), 0.69 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 174.9 (u), 137.0 (u), 129.2 (dn), 128.0 (dn), 126.6 (dn), 60.6 (u), 36.4 (u), 32.0 (dn), 30.6 (u), 28.1 (dn), 26.2 (u), 22.6 (dn), 22.1 (dn), 18.0 (u), 14.2 (dn); IR ($CHCl_3$, cm^{-1}): 3020, 2957, 1708, 1499, 1459, 1384, 1216, 1158, 1082, 1026, 757, 699, 669; HRMS-ESI m/z: [M + Na], calcd for $C_{17}H_{24}O_2Na$, 283.1674; found 283.1669.

(1*S*,2*R*)-(+)-Ethyl 1-butyl-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (6)



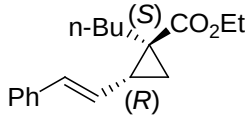
General procedure II was followed with 30 mg (0.22 mmol) of 4-vinylanisole (97% purity) and 75 mg (0.44 mmol) of ethyl 2-diazohexanoate to give 51 mg (0.18 mmol, 82%) of **6** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and only 1 peak was detected by GC analysis. The enantiomeric excess was measured to be 90% ee by HPLC analysis of the alcohol adduct obtained upon DIBAL reduction of the ester. A similar experiment starting with 65 mg (0.47 mmol) of 4-vinylanisole (97% purity) and 240 mg (1.41 mmol) of ethyl 2-diazohexanoate gave 104 mg (0.38 mmol, 81%) of **6**. Two peaks were detected in a > 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 91% by HPLC analysis. $[\alpha]^{20}_{D}$ = +78° (*c*. 1.04 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.09 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.22-4.10 (m, 2H), 3.80 (s, 3H), 2.69 (dd, *J* = 9.3 Hz, 7.2 Hz, 1H), 1.68-1.55 (m, 2H), 1.34-1.22 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.19-1.10 (m, 3H), 0.83-0.73 (m, 1H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 175.1 (u), 158.3 (u), 130.2 (dn), 129.1 (u), 113.5 (dn), 60.5 (u), 55.2 (dn), 31.5 (dn), 30.4 (u), 29.7 (u), 28.1 (u), 22.8 (u), 18.1 (u), 14.2 (dn), 13.9 (dn); IR ($CHCl_3$, cm^{-1}): 3011, 2959, 2873, 1706, 1612, 1515, 1463, 1380, 1318, 1292, 1249, 1203, 1174, 1059, 1035, 837, 736, 667; HRMS-ESI m/z: [M + Na], calcd for $C_{17}H_{24}O_3Na$, 299.1623; found 299.1618.

(1*S*,2*R*)-(+)-Ethyl 1-butyl-2-(4-fluorophenyl)cyclopropane-1-carboxylate (7)



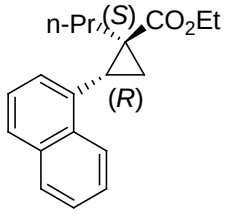
General procedure II was followed with 56 mg (0.45 mmol) of 4-fluorostyrene (97% purity) and 228 mg (1.34 mmol) of ethyl 2-diazohexanoate to give 118 mg (0.45 mmol, 100%) of known compound **7** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. Two peaks were detected in a 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 96% ee by HPLC analysis of the alcohol adduct obtained upon DIBAL reduction of the ester. A similar experiment starting with 49 mg (0.39 mmol) of 4-fluorostyrene (97% purity) and 200 mg (1.18 mmol) of ethyl 2-diazohexanoate gave 104 mg (0.39 mmol, 100%) of **7**. Two peaks were detected in a > 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 97% ee by HPLC analysis. $[\alpha]^{20}_{D}$ = +82° (*c*. 1.28 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

(1*S*,2*R*)-(+)-Ethyl 1-butyl-2-(*E*)-(β)-styrylcyclopropane-1-carboxylate (8)



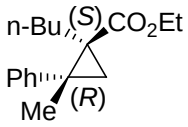
General procedure II was followed with 53 mg (0.41 mmol) of (*E*)-1-phenylbutadiene and 209 mg (1.23 mmol) of ethyl 2-diazohexanoate to give 77 mg (0.28 mmol, 68%) of **8** as a colorless oil. The purity was measured to be 93% by ^{1}H NMR. Two peaks were detected in a 96:4 ratio by GC analysis. The enantiomeric excess was measured to be 85% ee by HPLC analysis (CHIRACEL OD column, 0.2% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 55 mg (0.42 mmol) of (*E*)-1-phenylbutadiene and 214 mg (1.26 mmol) of ethyl 2-diazohexanoate gave 86 mg (0.32 mmol, 76%) of **8**. Two peaks were detected in a 97:3 ratio by GC analysis. The enantiomeric excess was measured to be 85% ee by HPLC analysis. $[\alpha]^{20}_{D}$ = +56° (*c*. 0.84 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.36-7.27 (m, 4H), 7.25-7.18 (m, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 5.98 (dd, *J* = 16.0 Hz, 8.4 Hz, 1H), 4.15 (dq, *J* = 7.1 Hz, 1.1 Hz, 2H), 2.30 (app q, *J* = 8.6 Hz, 1H), 2.73-2.65 (m, 1H), 1.61-1.57 (m, 1H), 1.56-1.50 (m, 1H), 1.49-1.41 (m, 2H), 1.33-1.23 (m, 5H), 0.96-0.87 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 174.6 (u), 137.3 (u), 132.3 (dn), 128.6 (dn), 127.9 (dn), 127.2 (dn), 125.9 (dn), 60.6 (u), 30.8 (u), 30.1 (dn), 30.0 (u), 29.0 (u), 22.9 (u), 21.6 (u), 14.2 (dn), 14.0 (dn); IR ($CHCl_3$, cm^{-1}): 3014, 2959, 2872, 1709, 1450, 1382, 1244, 1207, 1176, 1156, 1044, 961, 758, 747, 694, 667; HRMS-CI(NH_3) m/z: [M+H], calcd for $C_{18}H_{25}O_2$, 273.1855; found 273.1865.

(1*S*,2*R*)-(–)-Ethyl 2-(naphthalen-1-yl)-1-propylcyclopropane-1-carboxylate (9)



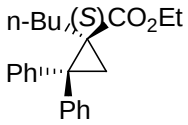
General procedure II was followed with 31 mg (0.19 mmol) of 1-vinylnaphthalene (95% purity) and 89 mg (0.57 mmol) of ethyl 2-diazopentanoate to give 41 mg (0.15 mmol, 79%) of **9** as a pale yellow oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. Two peaks were detected in a 98:2 ratio by GC analysis. The enantiomeric excess was measured to be 93% ee by HPLC analysis of the alcohol adduct obtained upon DIBAL reduction of the ester. A similar experiment starting with 70 mg (0.43 mmol) of 1-vinylnaphthalene (95% purity) and 201 mg (1.28 mmol) of ethyl 2-diazopentanoate gave 85 mg (0.30 mmol, 70%) of **9**. Two peaks were detected in a 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 94% ee by HPLC analysis. $[\alpha]^{20}_{D} = -113°$ (*c*. 1.60 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 8.04 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.56-7.48 (m, 2H), 7.41 (t, *J* = 7.1, 1H), 7.30-7.24 (m, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.01 (dd, *J* = 8.8 Hz, 7.7 Hz, 1H), 1.90 (m, 1H), 1.75-1.66 (m, 1H), 1.43-1.32 (m, 2H), 1,38 (t, *J* = 7.1 Hz, 3H), 1.30-1.19 (m, 1H), 0.66 (t, J= 7.4 Hz, 3H), 0.47-0.38 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 175.1 (u), 134.1 (u), 133.5 (u, 2 carbons), 128.4 (dn), 127.5 (dn), 126.2 (dn), 126.1 (dn), 125.8 (dn), 125.2 (dn), 124.2 (dn), 60.7 (u), 30.6 (u), 30.4 (u), 30.4 (dn), 20.9 (u), 17.6 (u), 14.4 (dn), 14.1 (dn); IR ($CHCl_3$, cm^{-1}): 3011, 2963, 2873, 1708, 1463, 1374, 1294, 1226, 1177, 1138, 1054, 802, 749; HRMS-ESI m/z: [M + Na], calcd for $C_{19}H_{22}O_2Na$, 305.1518; found 305.1514.

(1*S*,2*R*)-(+)-Ethyl 1-butyl-2-methyl-2-phenylcyclopropane-1-carboxylate (10)



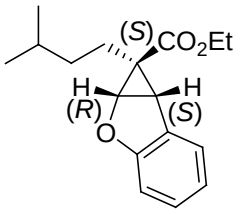
General procedure II was followed with 20 mg (0.17 mmol) of α-methylstyrene (99% purity) and 87 mg (0.51 mmol) of ethyl 2-diazohexanoate to give 39 mg (0.15 mmol, 88%) of known compound **10** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. Two peaks were detected in a 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 97% ee by HPLC analysis (CHIRACEL OD column, 0.1% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 51 mg (0.43 mmol) of α-methylstyrene (99% purity) and 217 mg (1.28 mmol) of ethyl 2-diazohexanoate gave 80 mg (0.41 mmol, 95%) of **10**. Two peaks were detected in a > 99:1 ratio by GC analysis. The enantiomeric excess was measured to be 96% ee by HPLC analysis. $[\alpha]^{20}_D$ = +50° (*c*. 0.56 $CHCl_3$); The spectral properties were identical to those previously described in the literature for the racemic material.[5]

(*S*)-(–)-Ethyl 1-butyl-2,2-diphenylcyclopropane-1-carboxylate (11)



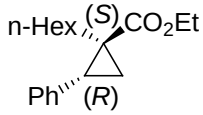
General procedure II was followed with 33 mg (0.18 mmol) of 1,1-diphenylethylene (97% purity) and 61 mg (0.36 mmol) of ethyl 2-diazohexanoate to give 53 mg (0.16 mmol, 89%) of **11** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR. The enantiomeric excess was measured to be 63% ee by HPLC analysis of the alcohol adduct obtained upon DIBAL reduction of the ester. A similar experiment starting with 80 mg (0.43 mmol) of 1,1-diphenylethylene (97% purity) and 219 mg (1.29 mmol) of ethyl 2-diazohexanoate gave 138 mg (0.43 mmol, 100%) of **11**. The enantiomeric excess was measured to be 63% ee by HPLC analysis. $[\alpha]^{20}_{D} = -5.2°$ (*c*. 0.90 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.39-7.33 (m, 4H), 7.22-7.19 (m, 2H), 7.17-7.10 (m, 3H), 7.08-7.01 (m, 1H), 3.83-3.75 (m, 1H), 3.72-3.65 (m, 1H), 2.38-2.28 (m, 1H), 2.24 (dd, *J* = 5.0 Hz, 1.5 Hz, 1H), 1.35 (d, *J* = 5.0 Hz, 1H), 1.34-1.11 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H), 0.75 (t, *J* = 7.2 Hz, 3H), 0.45 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 172.5 (u), 143.2 (u), 142.3 (u), 129.4 (dn), 128.9 (dn), 128.5 (dn), 128.2 (dn), 126.6 (dn), 126.4 (dn), 60.3 (u), 43.9 (u), 36.7 (u), 32.7 (u), 30.1 (u), 22.7 (u), 22.2 (u), 14.1 (dn), 13.7 (dn); IR ($CHCl_3$, cm^{-1}): 3029, 2958, 2930, 2872, 1710, 1494, 1449, 1373, 1263, 1087, 1025, 760, 748, 707; HRMS-ESI m/z: [M + Na], calcd for $C_{22}H_{26}O_2Na$, 345.1831; found 345.1829.

(1*R*,5*S*,6*S*)-(+)-3,4-Benzo-6-ethoxycarbonyl-6-isopentyl-2-oxabicyclo[3.1.0]hex-3-ene (**12**)



General procedure II was followed with 49 mg (0.41 mmol) of benzofuran and 228 mg (1.24 mmol) of ethyl 2-diazo-5-methylhexanoate to give 106 mg (0.39 mmol, 95%) of **12** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and GC. The diastereomer ratio was measured to be ≥ 95:5 by ^{1}H NMR, and only one peak was detected by GC analysis. The enantiomeric excess was measured to be 99% ee by HPLC analysis (CHIRACEL OD column, 0.1% isopropanol in hexanes, 1 mL/min, 220 nm). An identical experiment gave 106 mg (0.39 mmol, 95%) of **12**. The diastereomer ratio was measured to be ≥ 95:5 by ^{1}H NMR, and only one peak was detected by GC analysis. The enantiomeric excess was measured to be 99% ee by HPLC analysis. $[\alpha]^{20}_D$ = +240° (*c*. 0.84 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.35 (dd, *J* = 7.4 Hz, 1.4 Hz, 1H), 7.18 (app dt, *J* = 7.7 Hz, 1.5 Hz, 1H), 6.93 (app dt, *J* = 7.6 Hz, 1.3 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 5.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.33 (d, *J* = 5.7 Hz, 1H), 1.39-1.27 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.26-1.18 (m, 2H), 1.04-0.93 (m, 2H), 0.68 (d, *J* = 6.8 Hz, 3H), 0.55 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 173.6 (u), 161.4 (u), 128.1 (dn), 126.1 (u), 125.6 (dn), 121.2 (dn), 109.3 (dn), 70.9 (dn), 61.0 (u), 35.8 (u), 34.8 (dn), 28.0 (dn), 26.0 (u), 22.4 (dn), 21.9 (dn), 18.8 (u), 14.3 (dn); IR ($CHCl_3$, cm^{-1}): 2958, 2871, 1703, 1616, 1596, 1464, 1370, 1311, 1239, 1204, 1159, 1090, 1058, 1033, 758, 747; HRMS-CI(NH_3) m/z: [M+], calcd for $C_{17}H_{22}O_3$, 274.1569; found 274.1564.

(1*S*,2*R*)-(+)-Ethyl 1-hexyl-2-phenylcyclopropane-1-carboxylate (13)

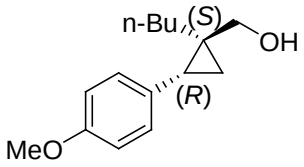


In a dry round bottomed flask, Rh_2(*S*-PTTL)$_4$ (2 mg, 0.001 mmol) and 85 mg (0.81 mmol) of styrene (99% purity) were dissolved in anhydrous hexanes (2.5 mL) and cooled by a bath of dry ice/acetone (−78°C) under a nitrogen atmosphere. Ethyl 2-diazooctanoate (54 mg, 0.27 mmol) was dissolved in hexanes (1.5 mL) and added to the reaction mixture via syringe pump at a rate of 1 mL/h. After the addition was complete, mesitylene (47 mg, 0.39 mmol) was added to the reaction mixture, and an ^{1}H NMR spectrum was taken to estimate the yield. The solvent was subsequently removed and the residue was chromatographed on silica gel to give 55 mg (0.20 mmol, 74%) of **13** as a colorless oil. The purity was measured to be ≥ 95% by ^{1}H NMR and only one peak was detected by GC analysis. The enantiomeric excess was measured to be 96% ee by HPLC analysis (CHIRACEL OD column, 0.2% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 82 mg (0.78 mmol) of styrene (99% purity) and 51 mg (0.26 mmol) of ethyl 2-diazooctanoate gave 49 mg (0.18 mmol, 69%) of **13**. Only one peak was detected by GC analysis. The enantiomeric excess was measured to be 95% ee by HPLC analysis. $[\alpha]^{20}_D$ = +82° (*c*. 0.93 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.32-7.26 (m, 2H), 7.24-7.17 (m, 3H), 4.25-4.13 (m, 2H), 2.77 (dd, *J* = 8.9 Hz, 6.8 Hz, 1H), 1.67 (dq, *J* = 4.8 Hz, 1.3 Hz, 1H), 1.63-1.53 (m, 1H), 1.33-1.26 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.20-1.06 (m, 7H), 0.89-0.79 (m, 1H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 175.0 (u), 137.3 (u), 129.2 (dn), 128.1 (dn), 126.6 (dn), 60.6 (u), 32.0 (dn), 31.6 (u), 30.5 (u), 29.4 (u), 28.5 (u), 27.4 (u), 22.5 (u), 17.9 (u), 14.2 (dn), 14.0 (dn); IR ($CHCl_3$, cm^{-1}): 2930, 1720, 1459, 1219, 1185, 1153, 772, 698; HRMS-ESI m/z: [M + Na], calcd for $C_{18}H_{26}O_2Na$, 297.1831; found 297.1825.

General procedure for ester reduction

To a dry round bottomed flask was added 0.10 mmol of the cyclopropane carboxylic ester in 0.7 mL anhydrous THF. The mixture was cooled by a bath of dry ice/acetone (–78 °C), and 0.39 mL (0.39 mmol) of a 1.0 M solution of diisobutylaluminium hydride in THF was added dropwise. The reaction mixture was then warmed to room temperature and allowed to stir for 1 hour. The flask was then cooled by a bath of ice water (0 °C) and 161 mg (0.50 mmol) $Na_2SO_4 \cdot 10H_2O$ was added and the mixture was allowed to warm to room temperature and stir for 30 minutes. The mixture was then filtered, concentrated, and chromatographed on silica gel.

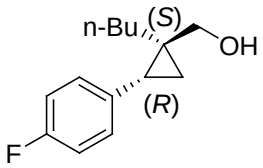
(1*S*,2*R*)-(+)-1-Butyl-2-(4-methoxyphenyl)cyclopropylmethanol (15)



The general procedure was followed starting with 18 mg (0.065 mmol) of **9** and 0.26 mL (0.26 mmol) of a 1.0 M diisobutylaluminium hydride solution to give 11 mg (0.047 mmol, 72%) of **15** as a colorless oil. The purity was measured to be > 95% by ^{1}H NMR. The enantiomeric excess was measured to be 90% ee by HPLC analysis (CHIRACEL OD column, 2% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 29 mg (0.11 mmol) of **9** and 0.43 mL (0.43 mmol) of diisobutylaluminium hydride solution gave 19 mg (0.081 mmol, 74%) of **15**. The enantiomeric excess was measured to be 91% ee by HPLC analysis. $[\alpha]^{20}_D$ = +21° (*c*. 0.50 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.09 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.68 (d, *J* = 10.2 Hz, 1H), 3.42 (d, *J* = 10.2 Hz, 1H), 2.01 (dd, *J* = 8.5 Hz, 5.9

Hz, 1H), 1.55 (bs, 1H), 1.32-1.22 (m, 3H), 1.20-1.06 (m, 2H), 0.96-0.88 (m, 1H), 0.87-0.80 (m, 2H), 0.77 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.8 (u), 130.7 (u), 130.0 (dn), 113.4 (dn), 69.1 (u), 55.2 (dn), 29.2 (u), 28.7 (u), 28.6 (u), 26.7 (dn), 22.9 (u), 14.2 (u), 14.0 (dn); IR ($CHCl_3$, cm^{-1}): 3613, 3457 (br), 3017, 2959, 2933, 2873, 1612, 1514, 1465, 1247, 1215, 1178, 1037, 909, 836, 757, 745, 735, 669; HRMS-CI(NH_3) m/z: [M^+], calcd for $C_{15}H_{22}O_2$, 234.1620; found 234.1611.

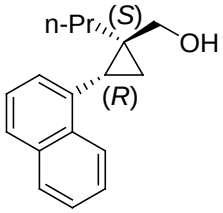
(1*S*,2*R*)-(–)-1-Butyl-2-(4-fluorophenyl)cyclopropylmethanol (16)



The general procedure for ester reduction was followed starting with 34 mg (0.13 mmol) of **10** and 0.52 mL (0.52 mmol) of a 1.0 M diisobutylaluminium hydride solution to give 14 mg (0.063 mmol, 48%) of **16** as a colorless oil. The purity was measured to be > 95% by ^{1}H NMR. The enantiomeric excess was measured to be 98% ee by HPLC analysis (CHIRACEL OD column, 2% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 44 mg (0.17 mmol) of **10** and 0.67 mL (0.67 mmol) of diisobutylaluminium hydride solution gave 19 mg (0.086 mmol, 51%) of **16**. The enantiomeric excess was measured to be 97% ee by HPLC analysis. $[\alpha]^{20}_D$ = –11° (*c*. 0.88 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.12 (dd, J = 8.7 Hz, 5.4 Hz, 2H), 6.93 (app t, J = 8.7 Hz, 2H), 3.67 (d, J = 11.3 Hz, 1H), 3.42 (d, J = 11.3 Hz, 1H), 2.02 (dd, J = 8.8 Hz, 7.0 Hz, 1H), 1.62 (bs, 1H), 1.33-1.20 (m, 3H), 1.20-1.02 (m, 2H), 0.98-0.89 (m, 2H), 0.88-0.83 (m, 1H), 0.75 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 161.3 (u)

[d, ^{1} (CF) = 243 Hz], 134.3 (u) [d, ^{4}J(CF) = 3 Hz], 130.4 (dn) [d, ^{3}J(CF) = 8 Hz], 114.7 (dn) [d, ^{2}J(CF) = 21 Hz], 68.8 (u), 29.3 (u), 28.6 (u, 2 carbons), 26.6 (dn), 22.9 (u), 14.4 (u), 13.9 (dn); IR ($CHCl_3$, cm^{-1}): 3452 (br), 3016, 2959, 2933, 2873, 1604, 1511, 1466, 1380, 1213, 1158, 1043, 1016, 840, 778, 767, 744, 669; HRMS-CI(NH_3) m/z: [M – CH_2OH], calcd for $C_{13}H_{16}F$, 191.1236; found 191.1238.

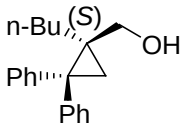
(1*S*,2*R*)-(–)-2-(Naphthalen-1-yl)-1-propylcyclopropylmethanol (17)



The general procedure was followed starting with 19 mg (0.071 mmol) of **12** and 0.27 mL (0.27 mmol) of a 1.0 M diisobutylaluminium hydride solution to give 12 mg (0.050 mmol, 75%) of **17** as a colorless oil. The purity was measured to be > 95% by ^{1}H NMR. The enantiomeric excess was measured to be 92% ee by HPLC analysis (CHIRACEL OD column, 2% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 26 mg (0.092 mmol) of **12** and 0.37 mL (0.37 mmol) of diisobutylaluminium hydride solution gave 18 mg (0.075 mmol, 82%) of **17**. The enantiomeric excess was measured to be 93% ee by HPLC analysis. $[\alpha]^{20}_{D}$ = –180° (*c*. 0.55 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.43 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.55-7.48 (m, 2H), 7.41-7.38 (m, 1H), 7.28-7.26 (m, 1H), 4.05 (d, *J* = 11.1 Hz, 1H), 3.59 (d, *J* = 11.1 Hz, 1H), 2.47 (dd, *J* = 8.5 Hz, 6.7 Hz, 1H), 1.61 (bs, 1H), 1.41-1.19 (m, 3H), 1.10-1.00 (m, 2H), 0.66 (t, *J* = 7.3 Hz, 3H), 0.61-0.52 (m, 1H); ^{13}C NMR

(100 MHz, $CDCl_3$, δ): 135.6 (u), 134.0 (u), 133.5 (u), 128.3 (dn), 126.8 (dn), 126.1 (dn), 125.8 (dn), 125.6 (dn), 125.3 (dn), 124.8 (dn), 69.0 (u), 31.1 (u), 28.9 (u), 25.8 (dn), 19.9 (u), 14.3 (dn), 13.6 (u); IR ($CHCl_3$, cm^{-1}): 3363 (br), 3020, 2961, 1510, 1422, 1215, 1045, 929, 757, 669, 627; HRMS-CI(NH_3) m/z: [M^+], calcd for $C_{17}H_{20}O$, 240.1514; found 240.1518.

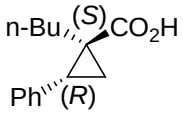
(*S*)-(+)-(1-Butyl-2,2-diphenylcyclopropyl)methanol (18)



The general procedure for ester reduction was followed starting with 45 mg (0.14 mmol) of **14** and 0.56 mL (0.56 mmol) of a 1.0 M diisobutylaluminium hydride solution to give 28 mg (0.10 mmol, 71%) of **18** as a colorless oil. The purity was measured to be > 95% by ^{1}H NMR. The enantiomeric excess was measured to be 63% ee by HPLC analysis (CHIRACEL OD column, 2% isopropanol in hexanes, 1 mL/min, 220 nm). A similar experiment starting with 31 mg (0.10 mmol) of **14** and 0.39 mL (0.39 mmol) of diisobutylaluminium hydride solution gave 22 mg (0.079 mmol, 79%) of **18**. The enantiomeric excess was measured to be 63% ee by HPLC analysis. $[\alpha]^{20}_D$ = +19° (*c*. 0.90 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.51 (dd, *J* = 8.5 Hz, 1.7 Hz, 2H), 7.42 (dd, *J* = 8.6 Hz, 1.5 Hz, 2H), 7.28-7.21 (m, 4H), 7.17-7.10 (m, 2H), 3.69 (d, *J* = 11.7 Hz, 1H), 3.19 (d, *J* = 11.7 Hz, 1H), 1.87-1.78 (m, 1H), 1.59-1.47 (m, 1H), 1.53-1.29 (m, 3H), 1.26-1.17 (m, 3H), 0.91-0.87 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 143.7 (u), 143.3 (u), 129.9 (dn), 129.5 (dn), 128.6 (dn), 128.3 (dn), 126.3 (dn), 126.1 (dn), 64.5 (u), 42.6 (u), 32.8 (u), 31.4 (u), 28.9 (u), 23.0 (u), 20.1 (u), 14.1 (dn); IR ($CHCl_3$, cm^-

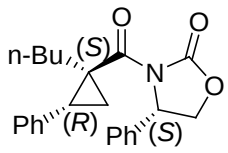
[1]): 3439 (br), 3023, 2958, 2932, 2860, 1493, 1461, 1379, 1033, 909, 773, 760, 709, 670; HRMS-CI(NH_3) m/z: [M – CH_2OH], calcd for $C_{19}H_{21}$, 249.1643; found 249.1641.

(1*S*,2*R*)-1-Butyl-2-phenylcyclopropanecarboxylic acid (19)



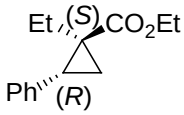
To a round bottom flask was added 43 mg (0.18 mmol) of **7** (96% ee) followed by 2 mL of 3:1 2.0 M KOH : EtOH. The mixture was heated to 90 °C for 16 hours. The mixture was then acidified with 3 M HCl, extracted with three 5 mL portions of CH_2Cl_2. The organic extracts were combined, dried (Na_2SO_4) and concentrated to give 39 mg (0.18 mmol, 100%) of **19** as a colorless oil. The purity of the crude material was measured to be 97% by ^{1}H NMR. It was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 11.0 (bs, 1H), 7.25-7.20 (m, 2H), 7.20-7.10 (m, 3H), 2.80 (dd, *J* = 9.2 Hz, 7.5 Hz, 1H), 1.68 (dq, *J* = 4.9 Hz, 1.0 Hz, 1H), 1.56-1.48 (m, 1H), 1.36-1.13 (m, 3H), 1.10-0.98 (m, 2H), 0.79-0.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 182.1 (u), 136.6 (u), 129.2 (dn), 128.2 (dn), 126.8 (dn), 33.2 (dn), 30.3 (u), 29.5 (u), 27.8 (u), 22.8 (u), 18.6 (u), 13.9 (dn).

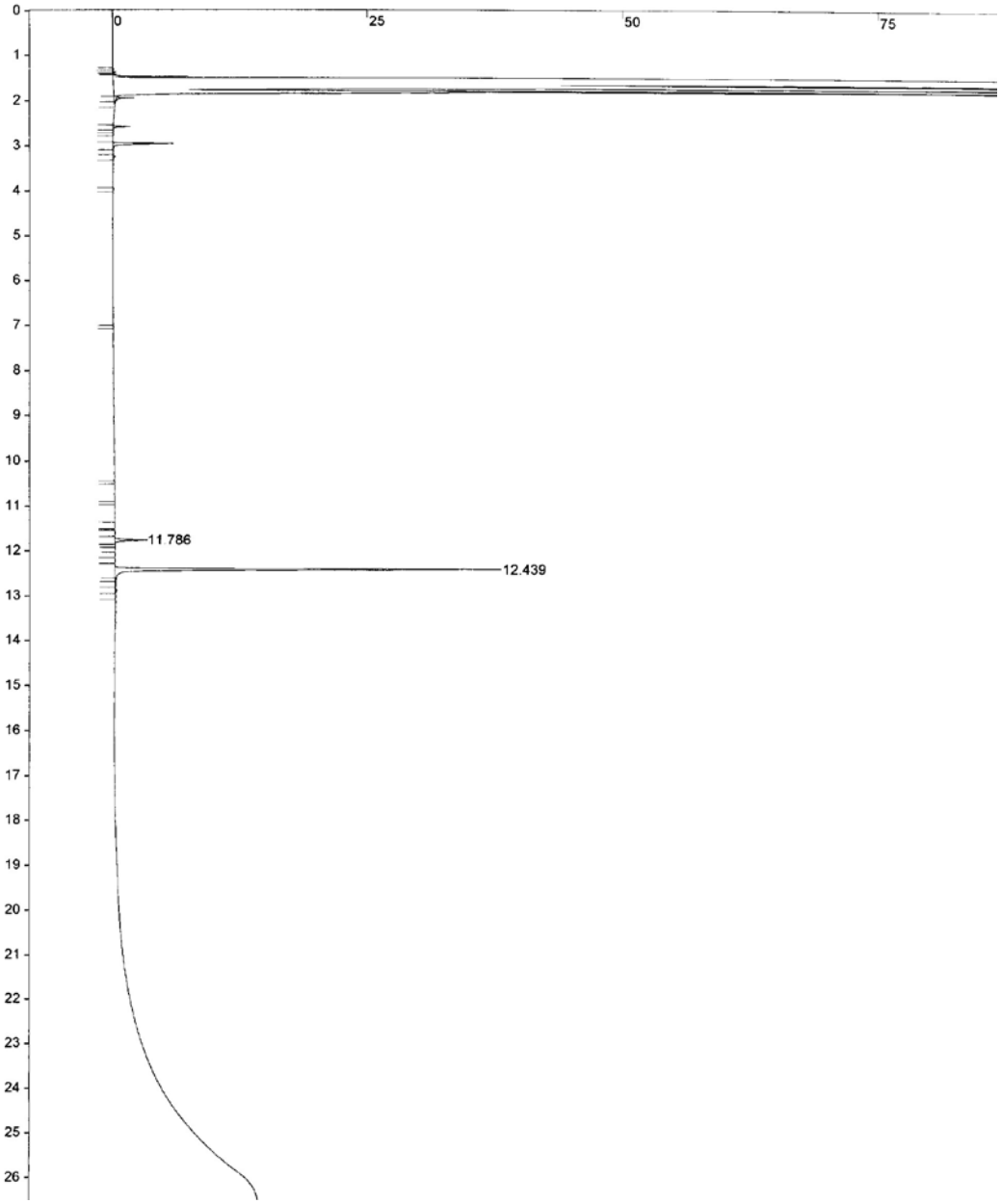
(1*S*,2*R*,3*S*)-(–)-1-Butyl-2-phenylcyclopropanecarbonyl-4-phenyloxazolidin-2-one (20)



To a dry round bottom flask was added 39 mg (0.18 mmol) **19** in 0.5 mL $SOCl_2$. The mixture was stirred at room temperature for 1 hour, and the excess $SOCl_2$ was subsequently removed *in vacuo*. Anhydrous THF (1.0 mL) was then added, followed by 44 mg (0.27 mmol) of (*S*)-(+)-4-phenyl 2-oxazolidinone and 63 μL Et_3N. The mixture was allowed to stir for 18 hours at room temperature. A white precipitate formed. The mixture was then added to 10 mL H_2O, and extracted with CH_2Cl_2 three times. The organic extracts were combined, dried ($MgSO_4$), concentrated and chromatographed on silica gel to give 44 mg (0.12 mmol, 67%) of **20** as a white solid, m.p. 90-91 °C. Small peaks attributable to impurities were observed at 5.57 ppm, 5.19 ppm, 4.80 ppm, 4.39 ppm, 2.61 ppm, 2.20 ppm, 1.12 ppm, and 0.44 ppm. X-ray quality crystals were grown from 1:1 Et_2O:hexanes. $[\alpha]^{20}_D = -56°$ (*c*. 0.50 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30-7.09 (m, 10H), 5.38 (dd, *J* = 8.9 Hz, 6.1 Hz, 1H), 4.61 (app t, *J* = 8.9 Hz, 1H), 4.22 (dd, *J* = 8.9 Hz, 6.3 Hz, 1H), 2.37 (dd, *J* = 9.4 Hz, 7.1 Hz, 1H), 1.83-1.74 (m, 1H), 1.65-1.57 (m, 1H), 1.02-0.88 (m, 5H), 0.81-0.70 (m, 1H), 0.55 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 174.3 (u), 152.7 (u), 138.3 (u), 136.5 (u), 129.9 (dn), 129.1 (dn), 128.9 (dn), 127.9 (dn), 126.9 (dn), 126.6 (dn), 69.8 (u), 58.6 (dn), 34.9 (u), 30.5 (dn), 30.0 (u), 28.8 (u), 22.6 (u), 14.9 (u), 13.9 (dn); IR ($CHCl_3$, cm^{-1}): 3023, 2928, 1787, 1688, 1460, 1383, 1324, 1225, 1201, 1047, 791, 700, 671; HRMS-ESI m/z: [M + Na], calcd for $C_{23}H_{25}NO_3Na$, 386.1732; found 386.1725.

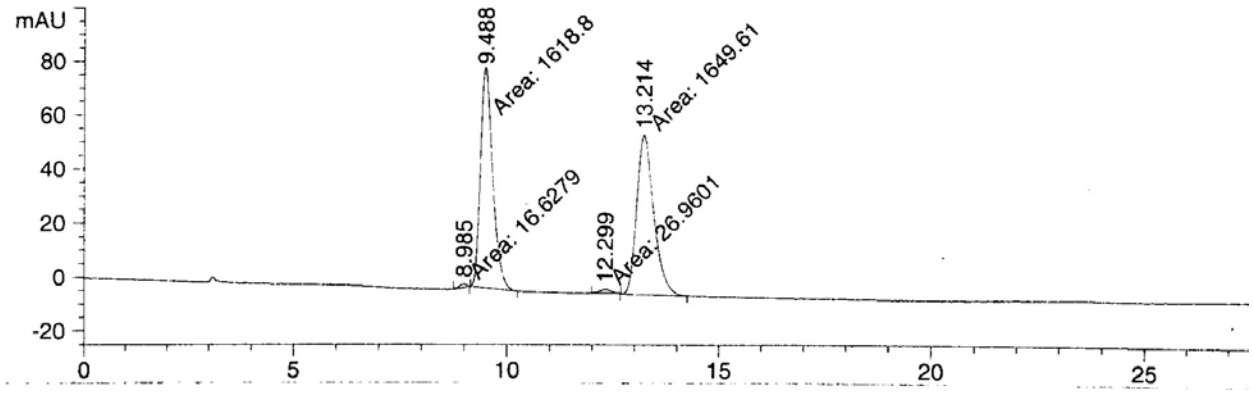
GC trace of **2** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)



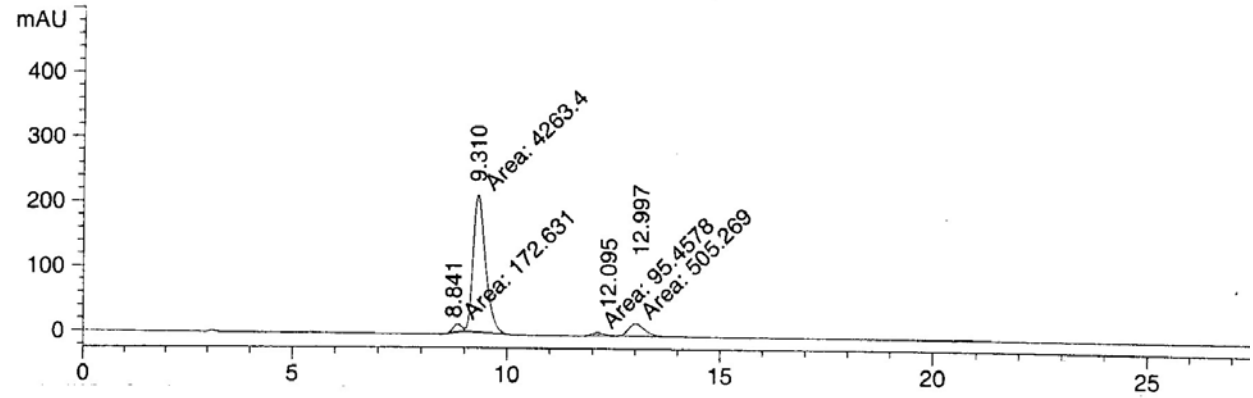


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		7.9160	11.786	0.000	7793	PP	2.2	
2		92.0840	12.439	0.000	90650	PB	2.1	
Totals:		100.0000		0.000	98443			

HPLC resolution of racemic **2** (Chiracel OD column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)

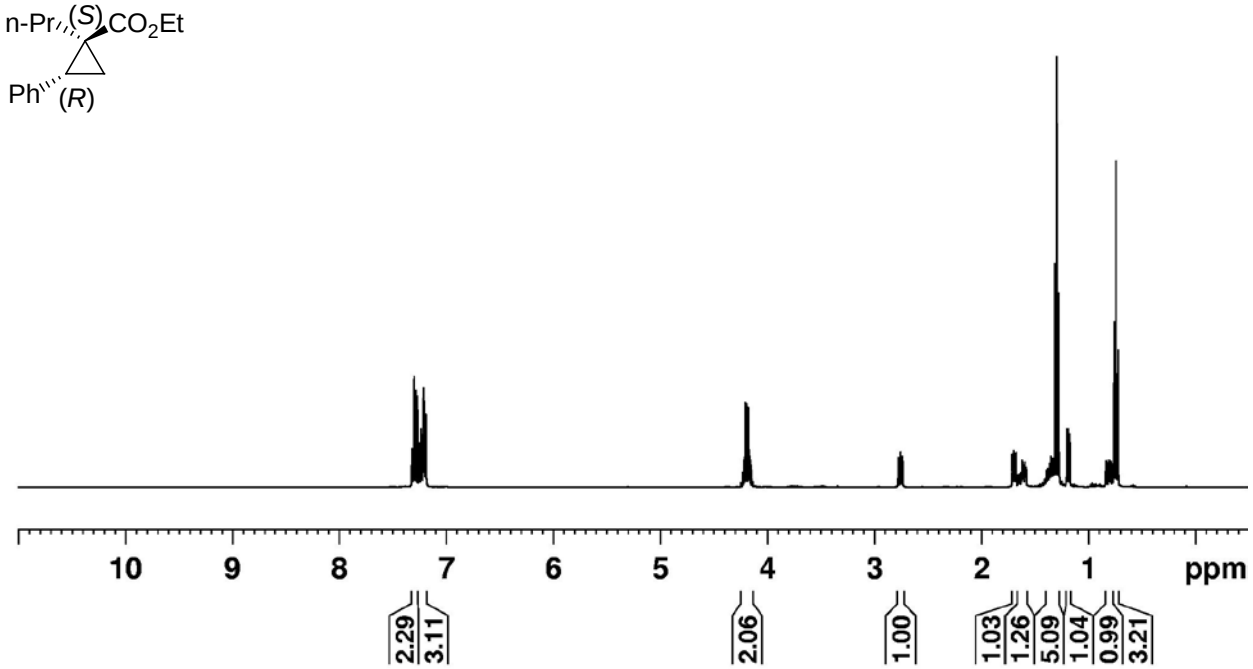


Enantiomeric excess of **2** (Chiracel OD column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)

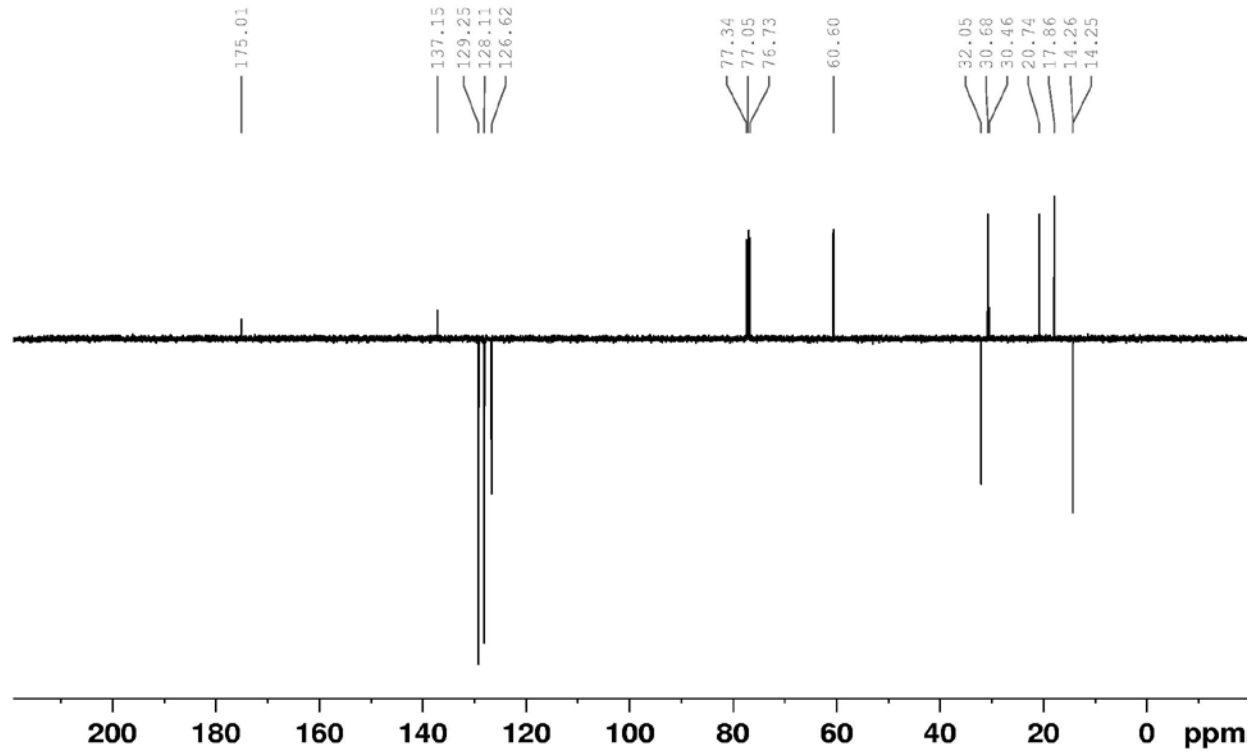


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.841	MM	0.2245	172.63121	12.81829	3.4274
2	9.310	MM	0.3363	4263.39990	211.31097	84.6457
3	12.095	MM	0.3612	95.45778	4.40508	1.8952
4	12.997	MM	0.4376	505.26917	19.24272	10.0316
Totals :				5036.75806	247.77707	

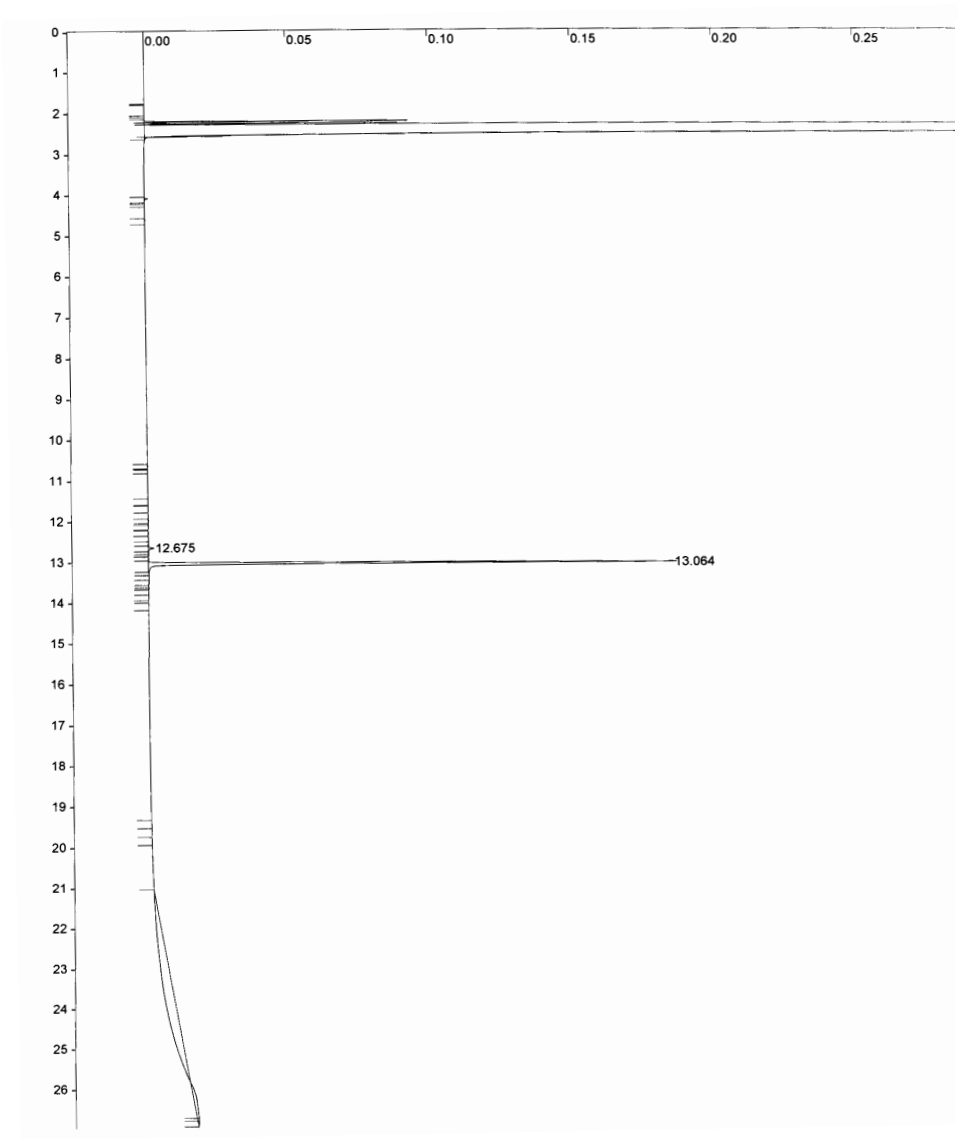
^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$)



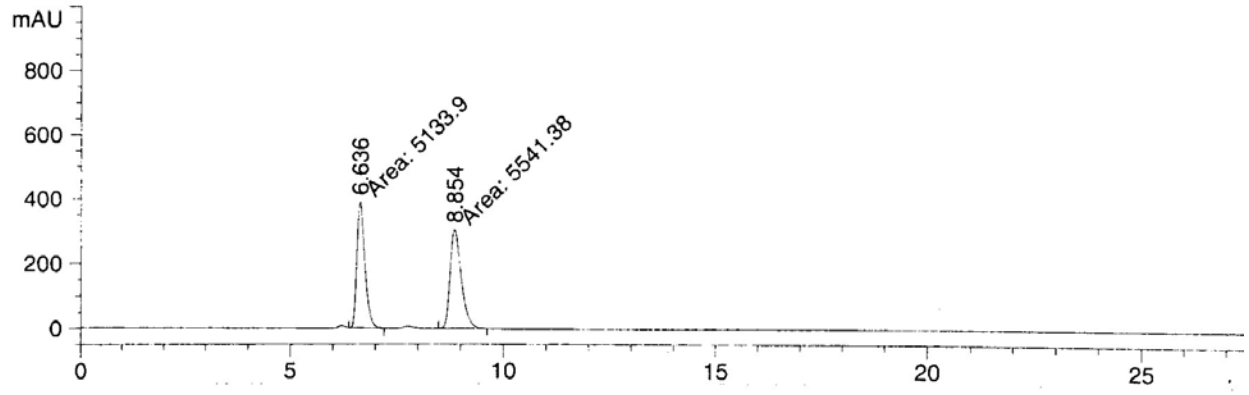
GC trace of **3** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)



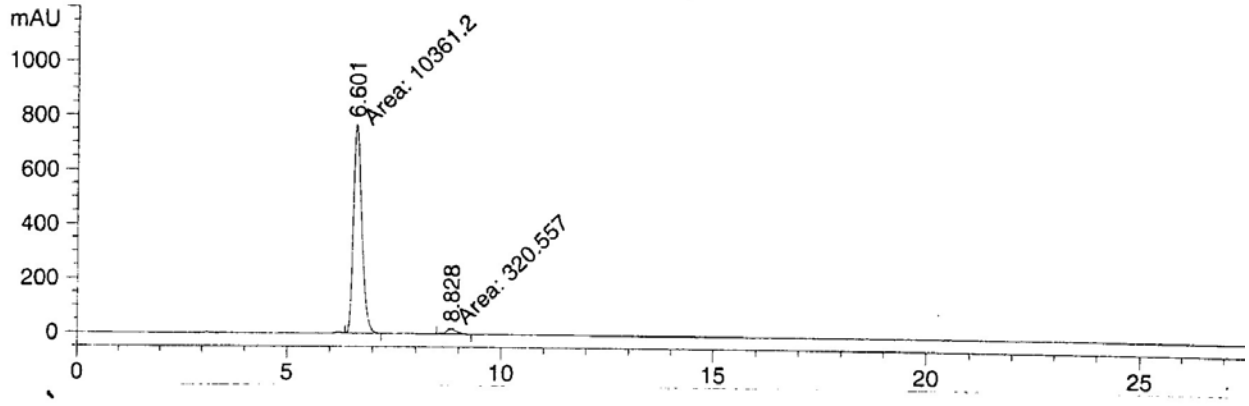
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		1.1995	12.675	0.000	5161	VP	2.2	
2		98.8005	13.064	0.000	425081	VB	2.1	
Totals:		100.0000		0.000	430242			

Total Unidentified Counts : 430242 counts

HPLC resolution of racemic **3** (Chiracel OD column, 99.8:0.2 hexanes:isopropanol, 1 mL/min, 220 nm)

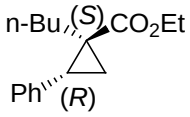


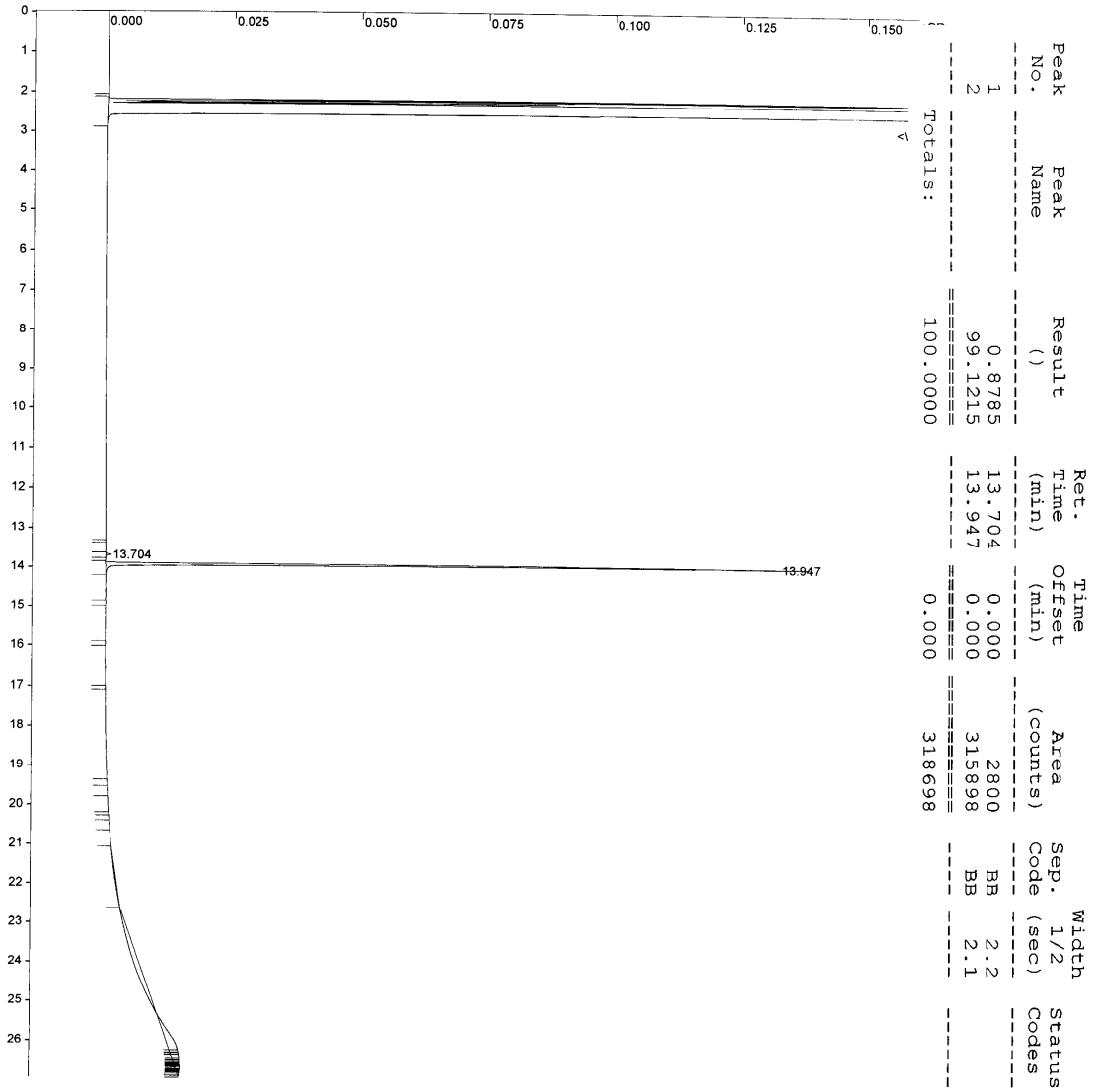
Enantiomeric excess of **3** (Chiracel OD column, 99.8:0.2 hexanes:isopropanol, 1 mL/min, 220 nm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.601	MM	0.2246	1.03612e4	768.95618	96.9990
2	8.828	MM	0.2755	320.55746	19.39226	3.0010
Totals :				1.06818e4	788.34843	

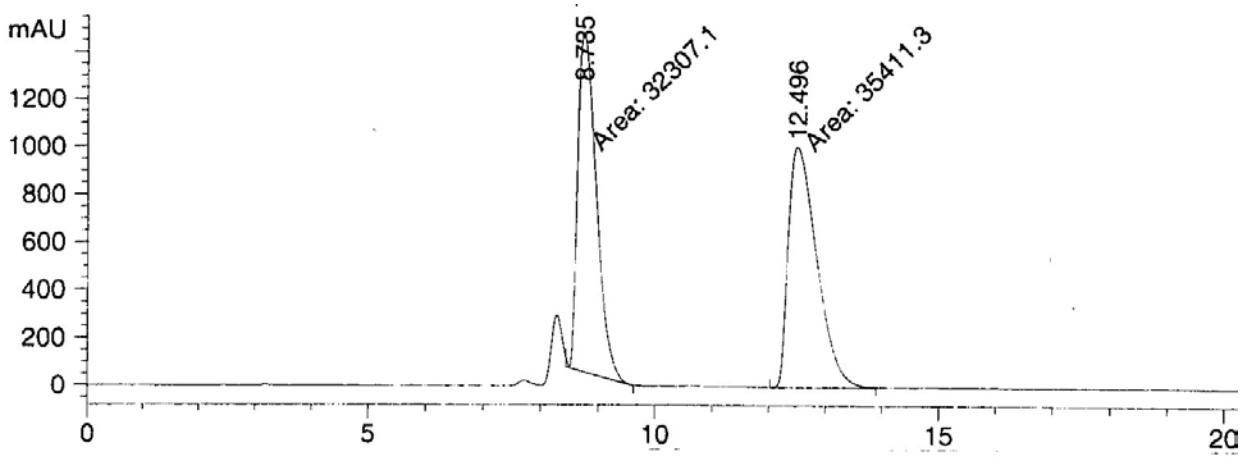
GC trace of **4** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)



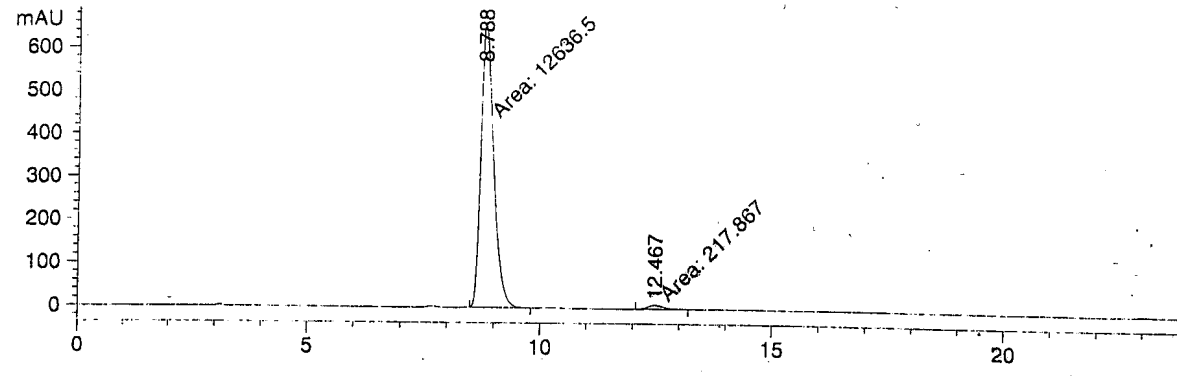


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.8785	13.704	0.000	2800	BB	2.2	
2		99.1215	13.947	0.000	315898	BB	2.1	
Totals:		100.0000		0.000	318698			

HPLC resolution of racemic **4** (Chiracel OD column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)

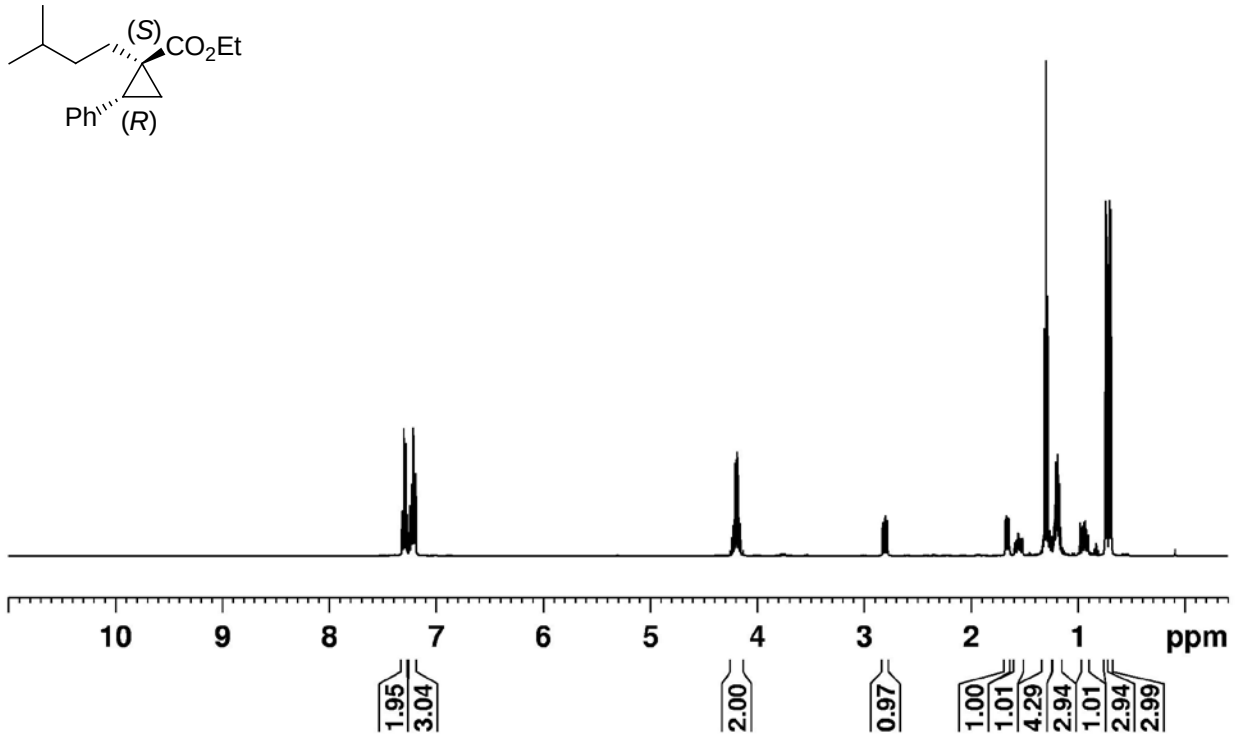


Enantiomeric excess of **4** (Chiracel OD column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)

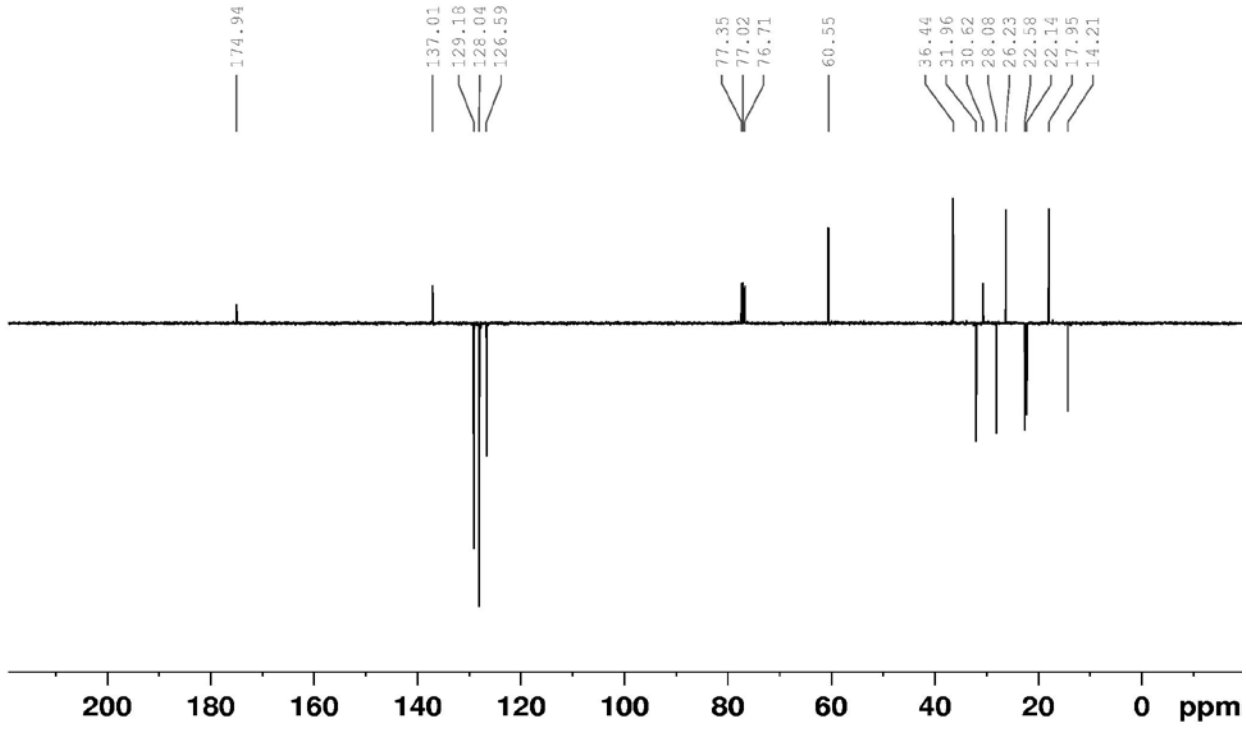


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.788	MM	0.3187	1.26365e4	660.85651	98.3051
2	12.467	MM	0.3976	217.86749	9.13299	1.6949
Totals :				1.28544e4	669.98949	

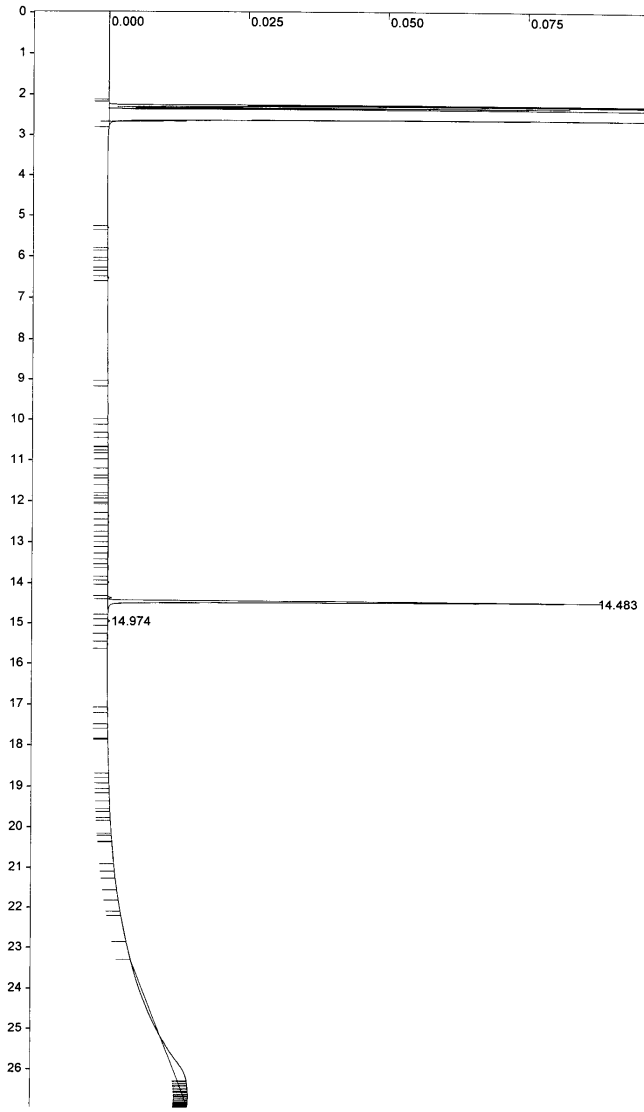
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$)

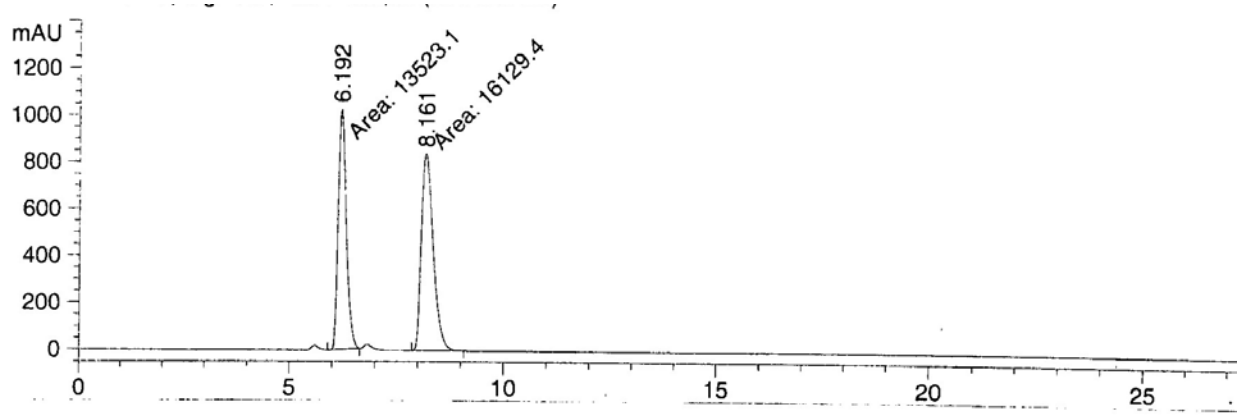


GC trace of **5** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)

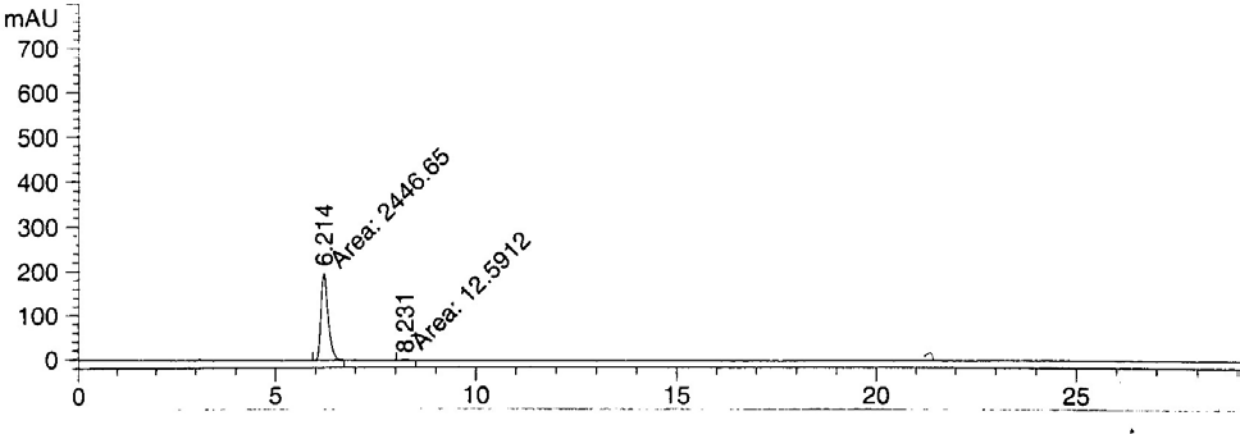


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		99.5273	14.483	0.000	205320	VB	2.1	
2		0.4727	14.974	0.000	975	BB	2.2	
Totals:		100.0000		0.000	206295			

HPLC resolution of racemic **5** (Chiracel OD column, 99.8:0.2 hexanes:isopropanol, 1 mL/min, 220 nm)

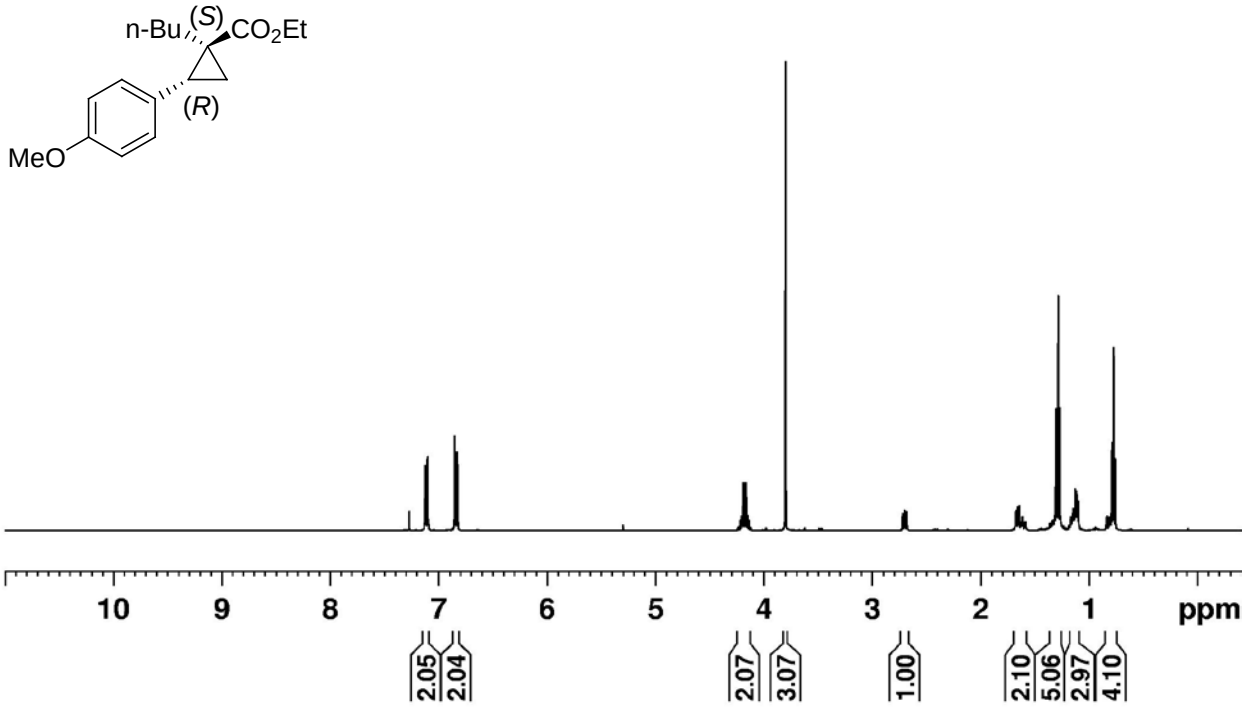


Enantiomeric excess of **5** (Chiracel OD column, 99.8:0.2 hexanes:isopropanol, 1 mL/min, 220 nm)

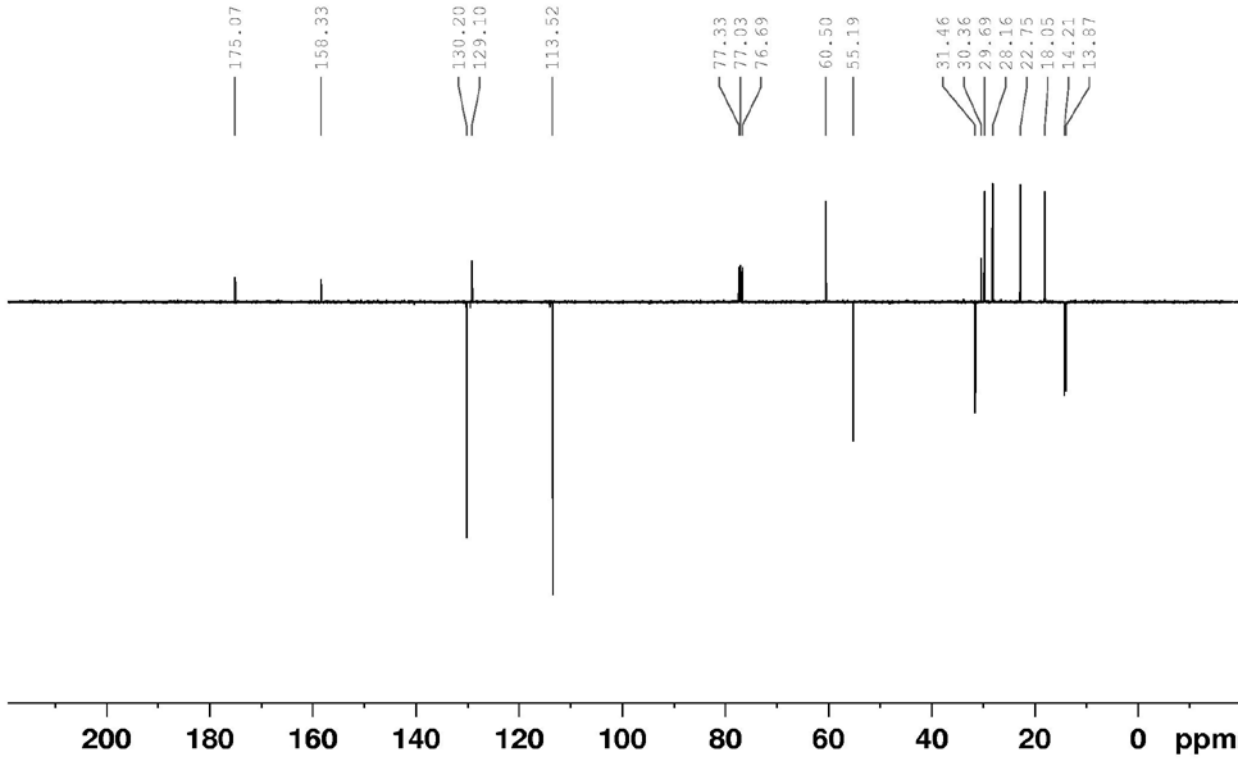


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.214	MM	0.2063	2446.64844	197.69658	99.4880
2	8.231	MM	0.2252	12.59121	9.31769e-1	0.5120
Totals :				2459.23964	198.62835	

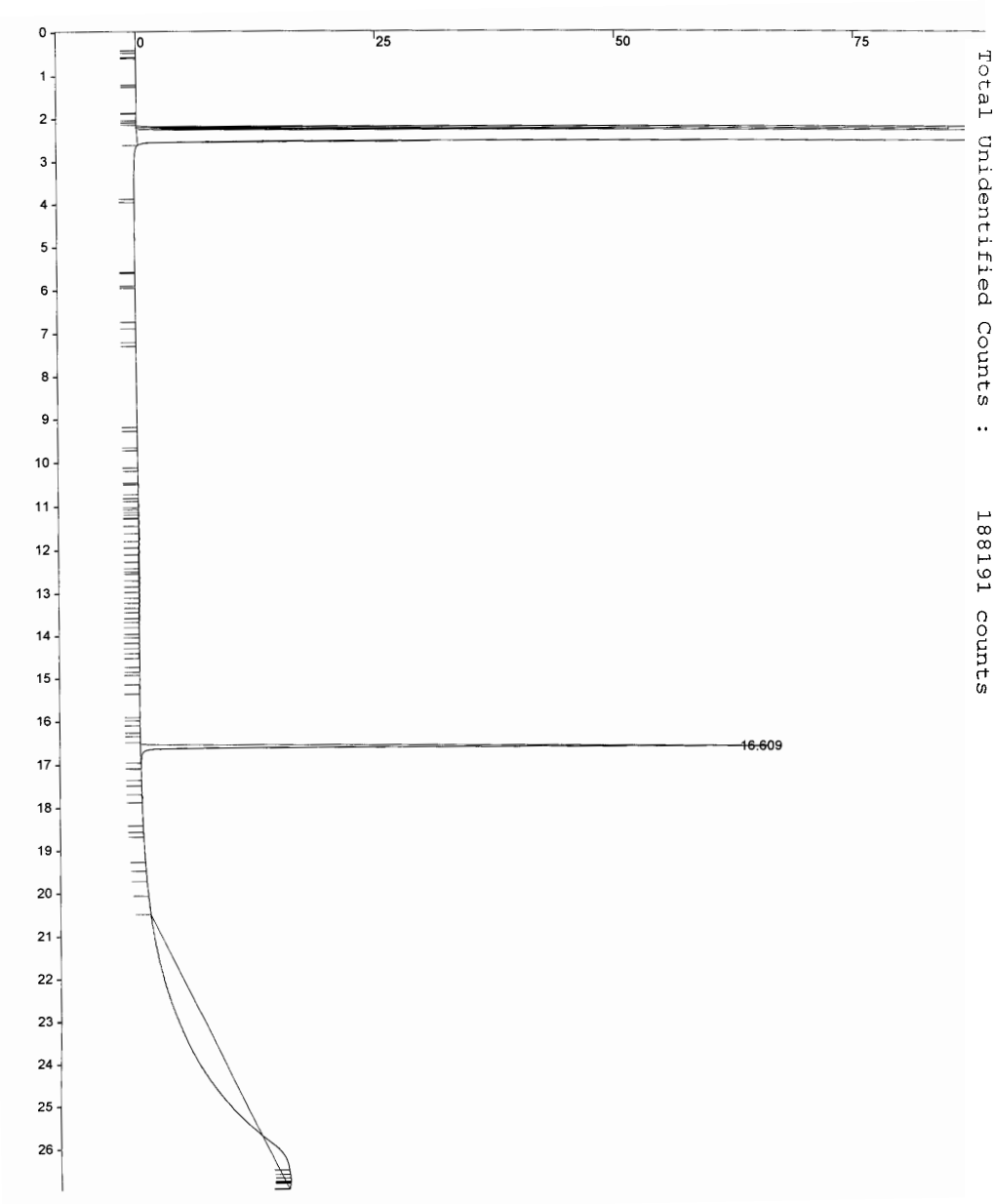
^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$)



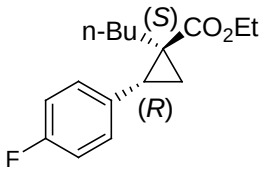
GC trace of **6** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)

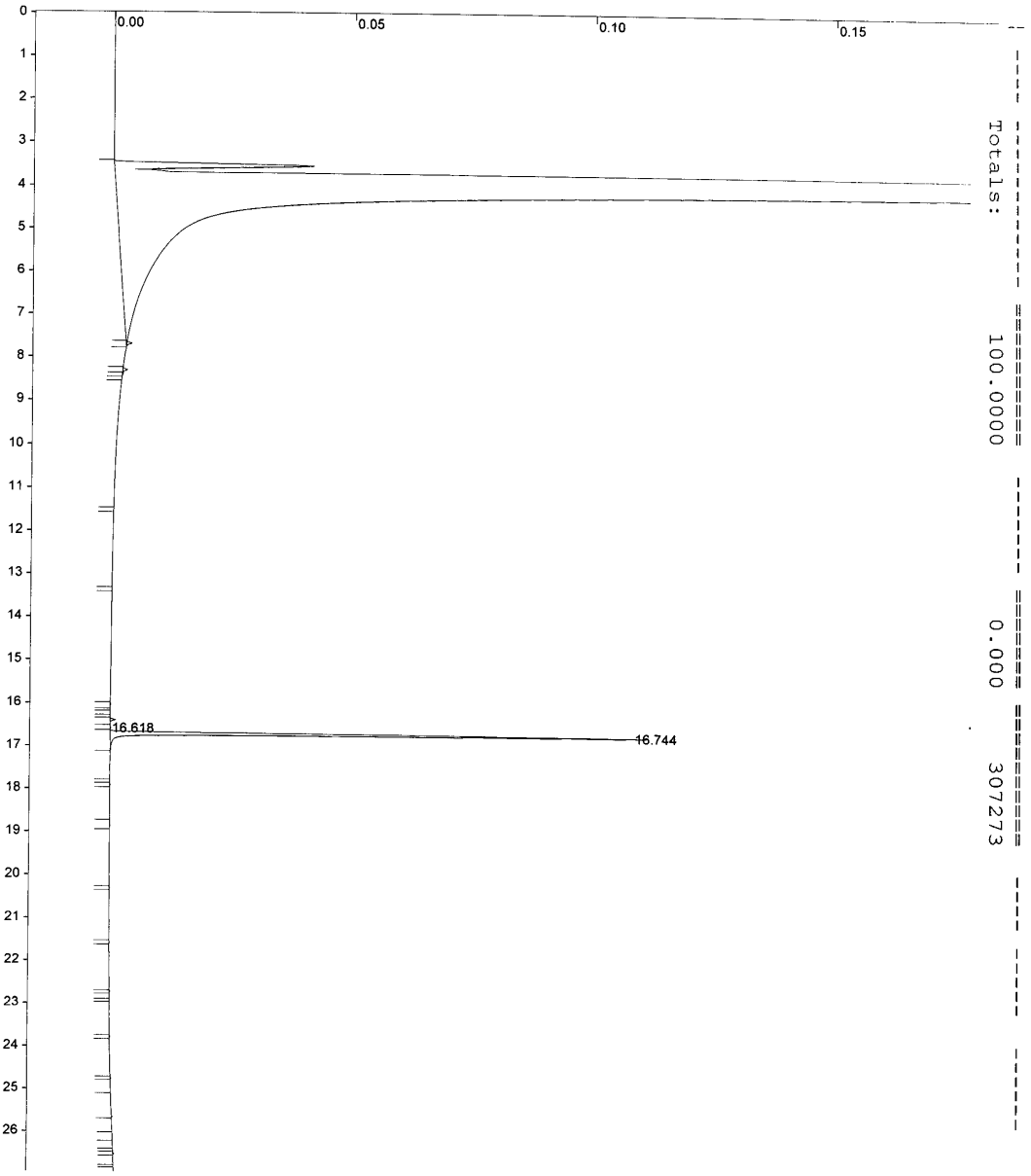


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	16.609	0.000	188191	BB	2.6	
Totals:		100.0000		0.000	188191			

Total Unidentified Counts : 188191 counts

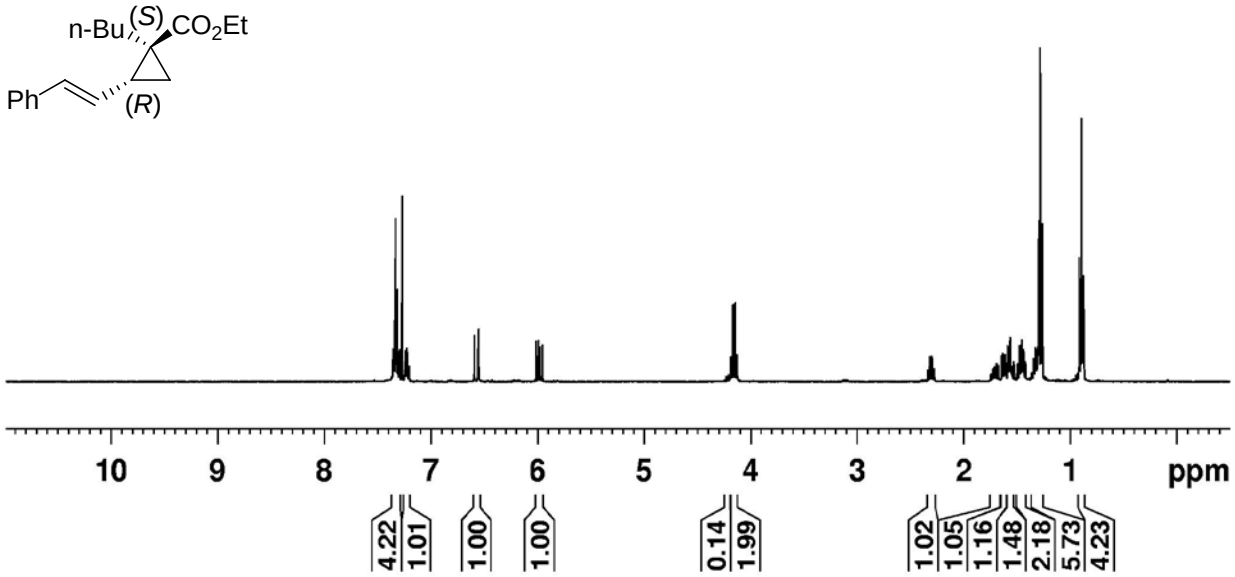
GC trace of **7** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)



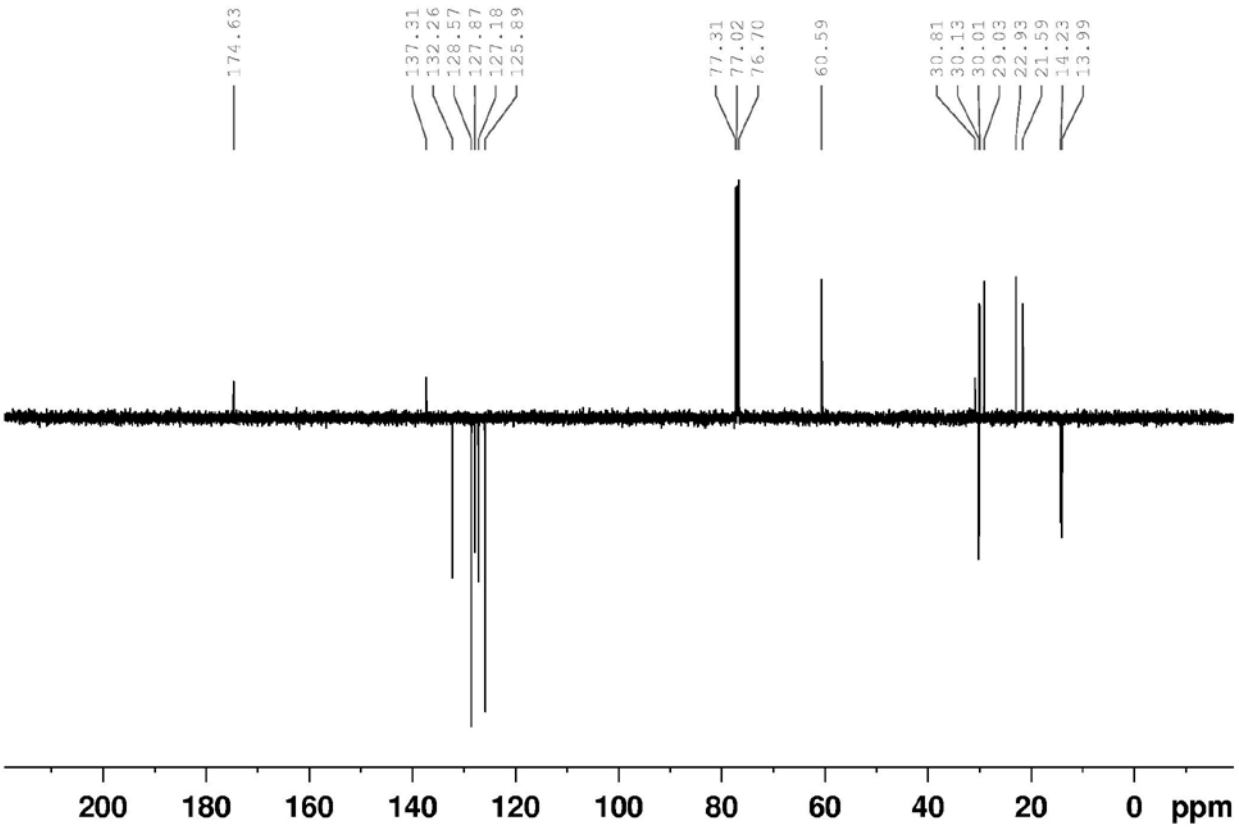


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		0.1038	16.618	0.000	319	PP	2.4	
2		99.8962	16.744	0.000	306954	PB	2.4	
Totals:		100.0000		0.000	307273			

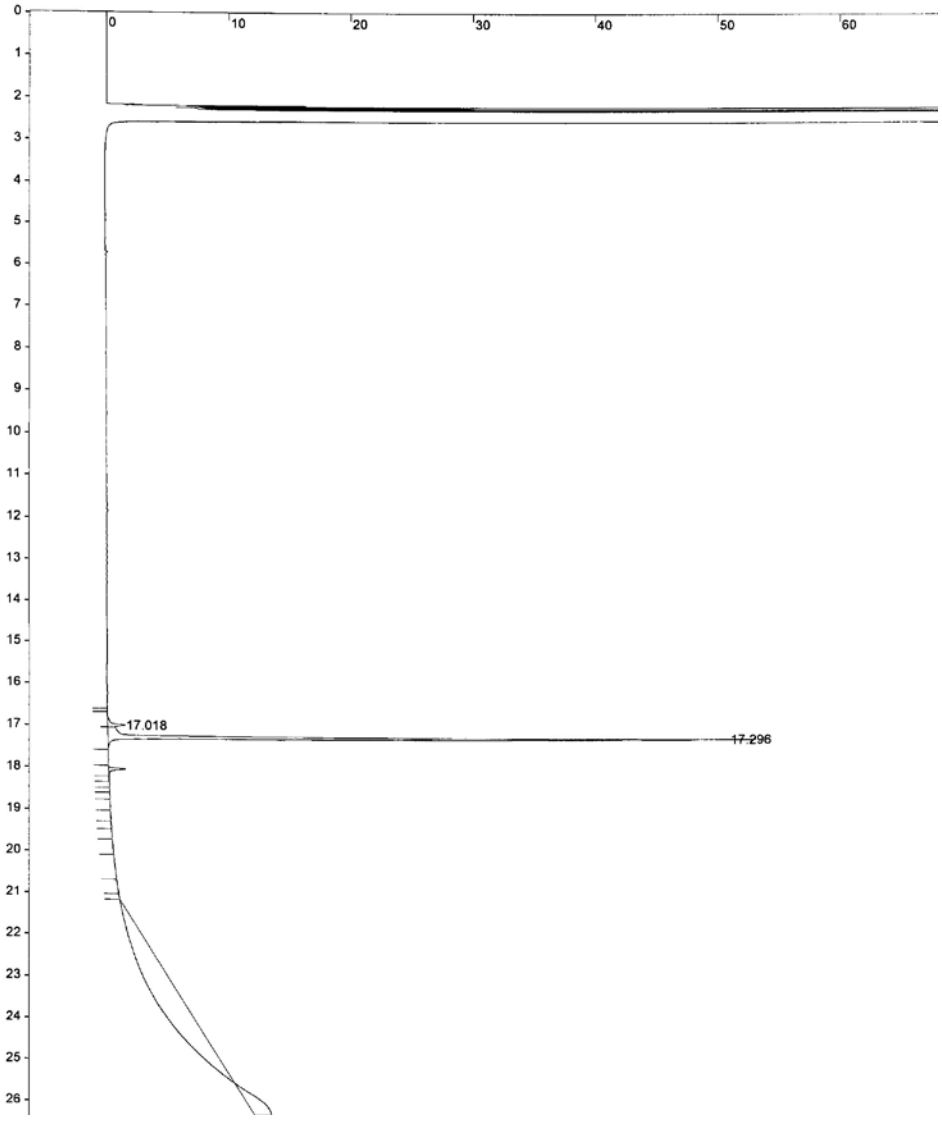
^{1}H NMR spectrum of **8** (400 MHz, $CDCl_3$) (93% purity)



^{13}C NMR spectrum of **8** (100 MHz, $CDCl_3$) (93% purity)

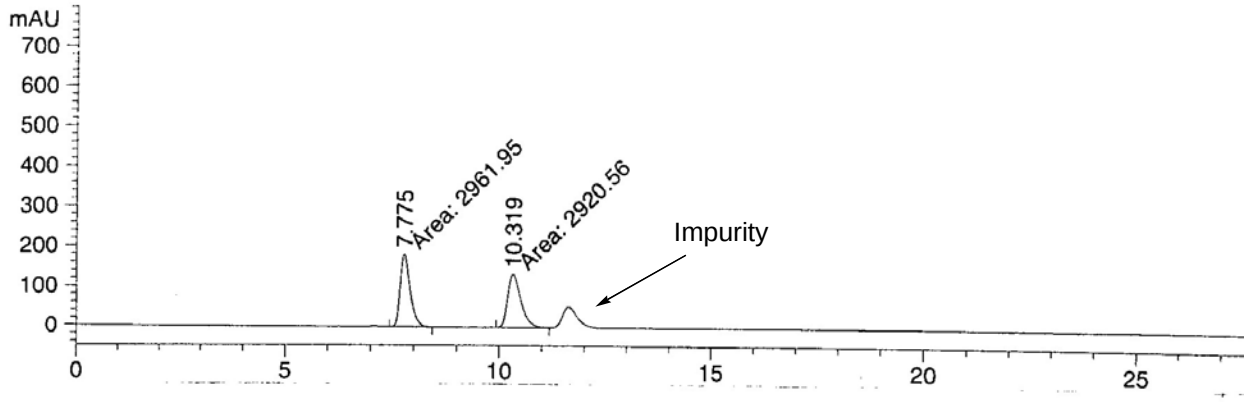


GC trace of **8** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)

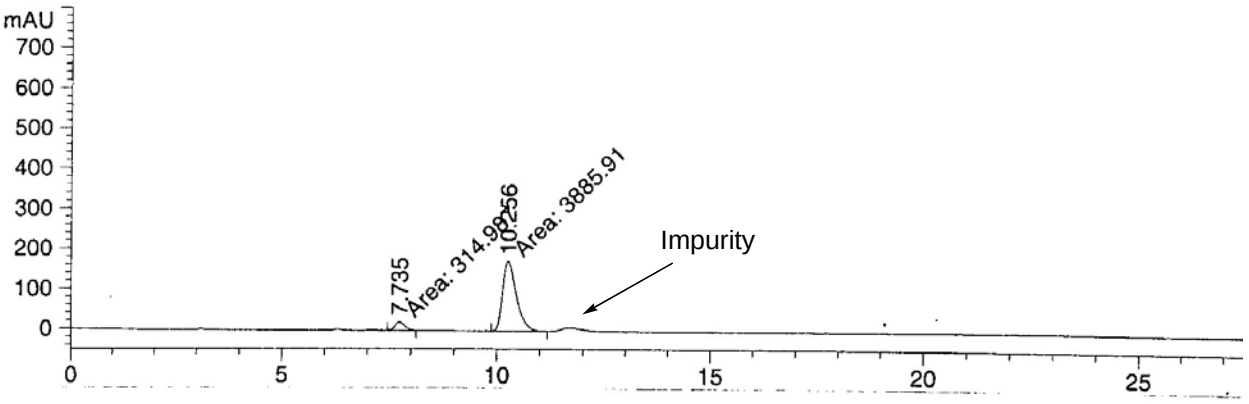


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		3.9407	17.018	0.000	6595	PV	3.8	
2		96.0593	17.296	0.000	160751	VB	2.6	
Totals:		100.0000		0.000	167346			

HPLC resolution of racemic **8** (Chiracel OD column, 99.8:0.2 hexanes:isopropanol, 1 mL/min, 220 nm)

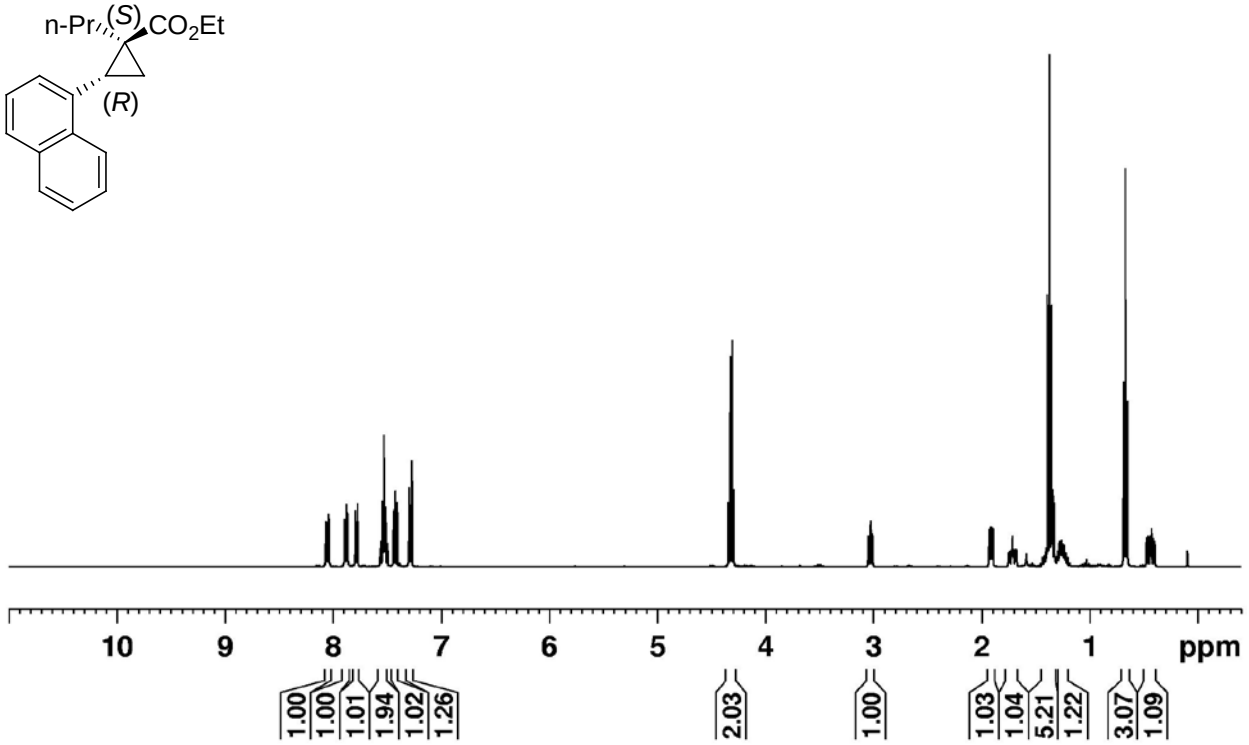


Enantiomeric excess of **8** (Chiracel OD column, 99.8:0.2 hexanes:isopropanol, 1 mL/min, 220 nm)

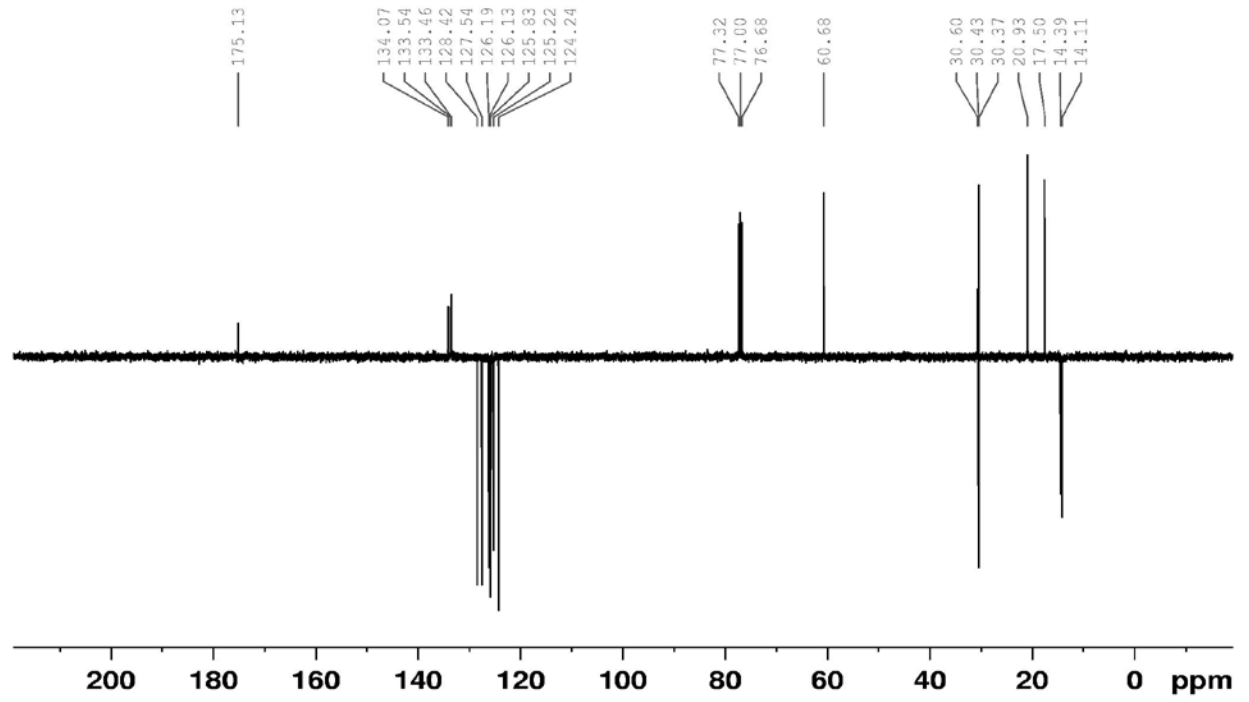


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.735	MM	0.2528	314.98734	20.76708	7.4981
2	10.256	MM	0.3726	3885.90942	173.83311	92.5019
Totals :				4200.89676	194.60020	

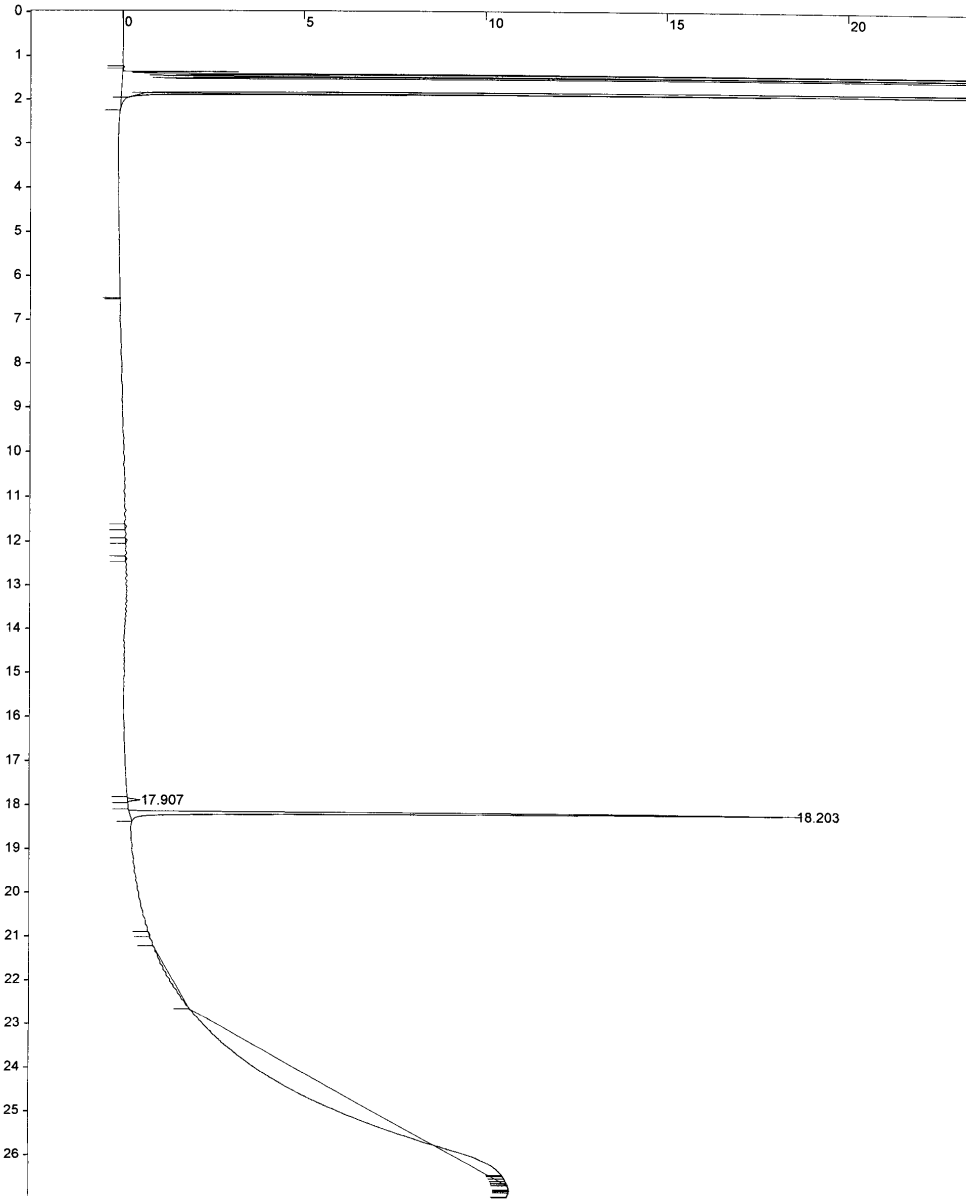
^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **9** (100 MHz, $CDCl_3$)



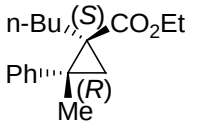
GC trace of **9** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)

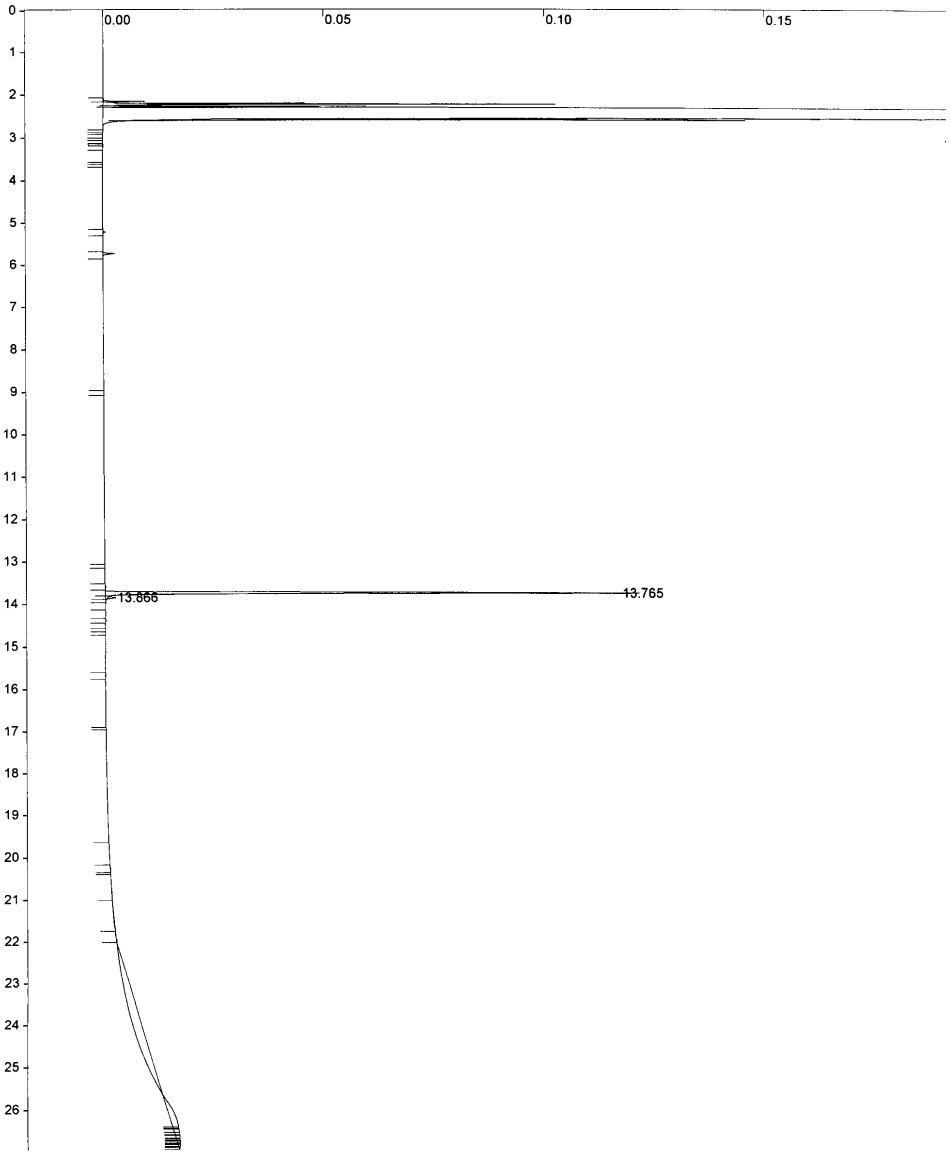


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		1.7993	17.907	0.000	974	BB	2.7	
2		98.2007	18.203	0.000	53152	BB	2.6	
Totals:		100.0000		0.000	54126			

Total Unidentified Counts : 54126 counts

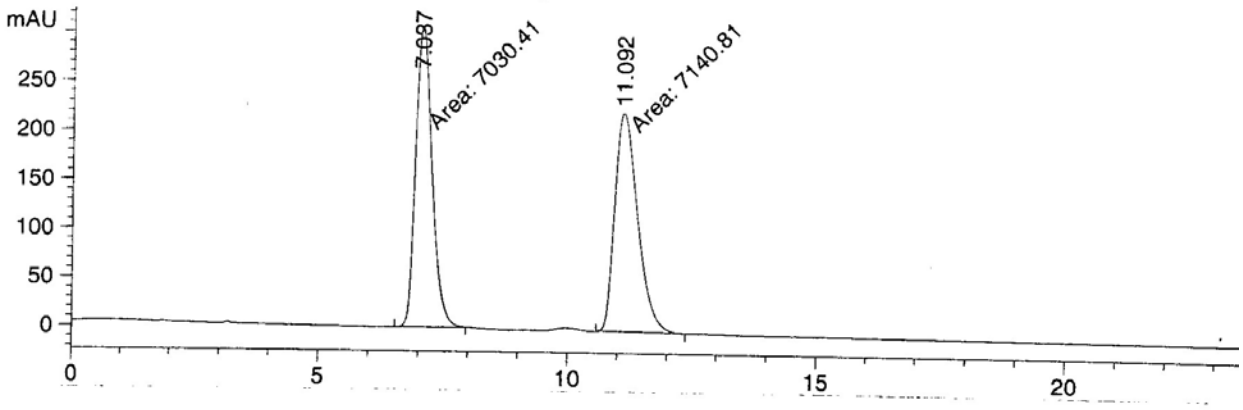
GC trace of **10** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)



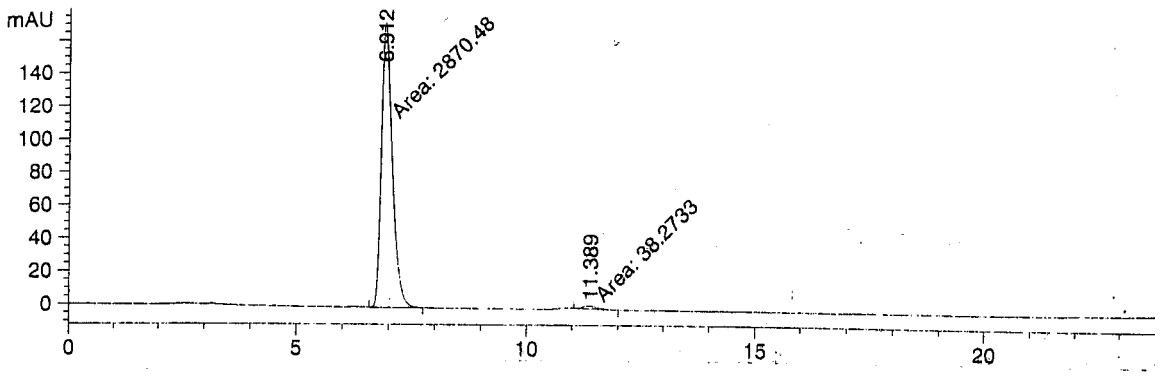


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		98.7880	13.765	0.000	280098	PB	2.1	
2		1.2120	13.866	0.000	3437	TS	0.0	
Totals:		100.0000		0.000	283535			

HPLC resolution of racemic **10** (Chiracel OD column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)

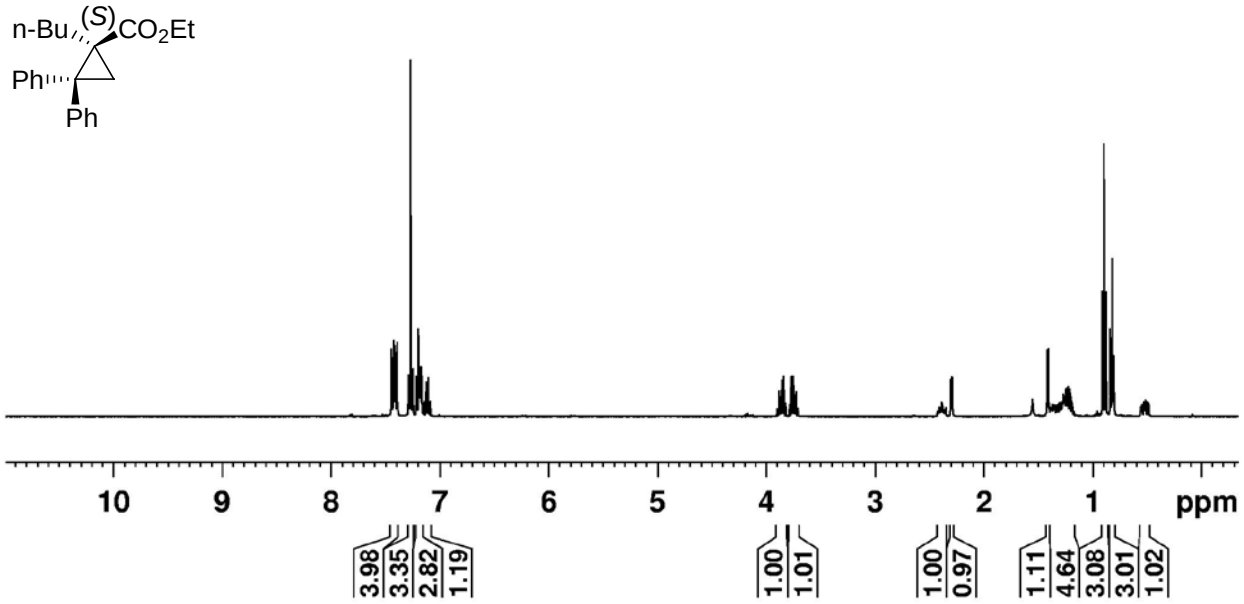


Enantiomeric excess of **10** (Chiracel OD column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)

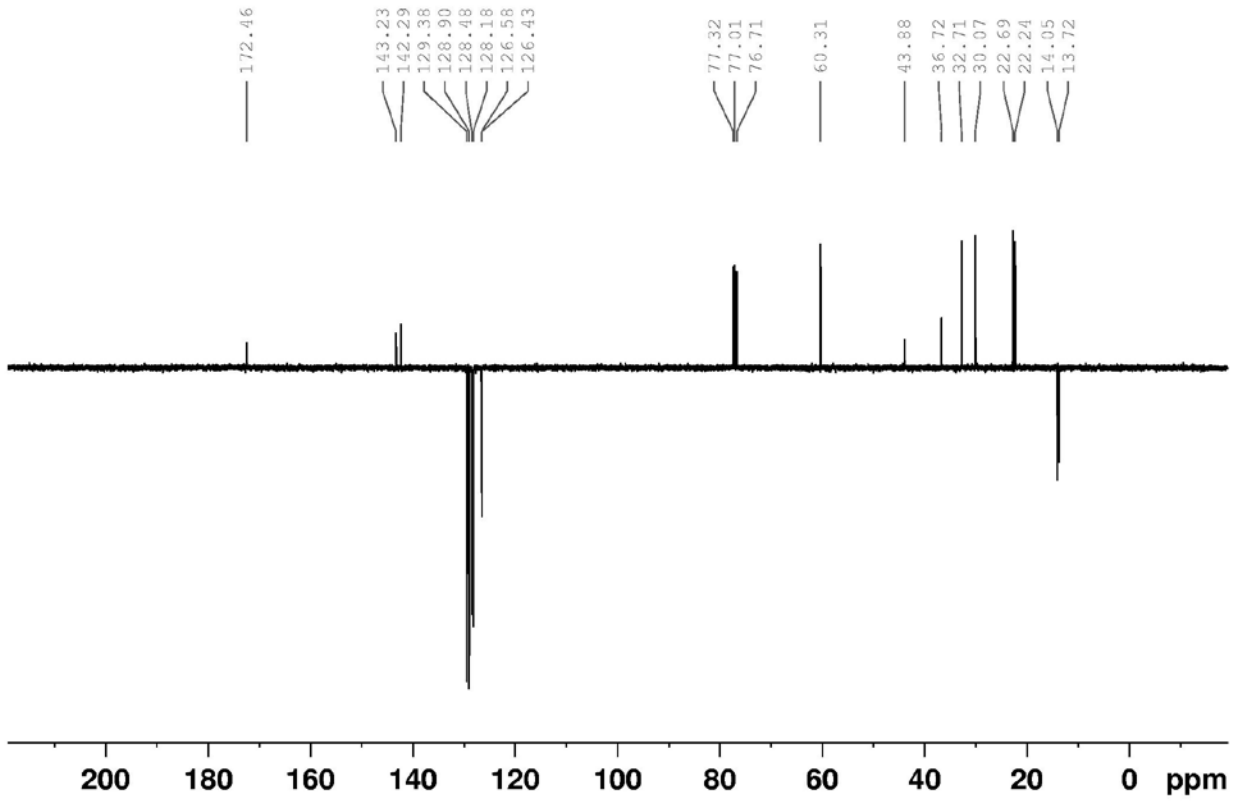


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.912	MM	0.2762	2870.47803	173.22308	98.6842
2	11.389	MM	0.3320	38.27334	1.92132	1.3158
Totals :				2908.75137	175.14440	

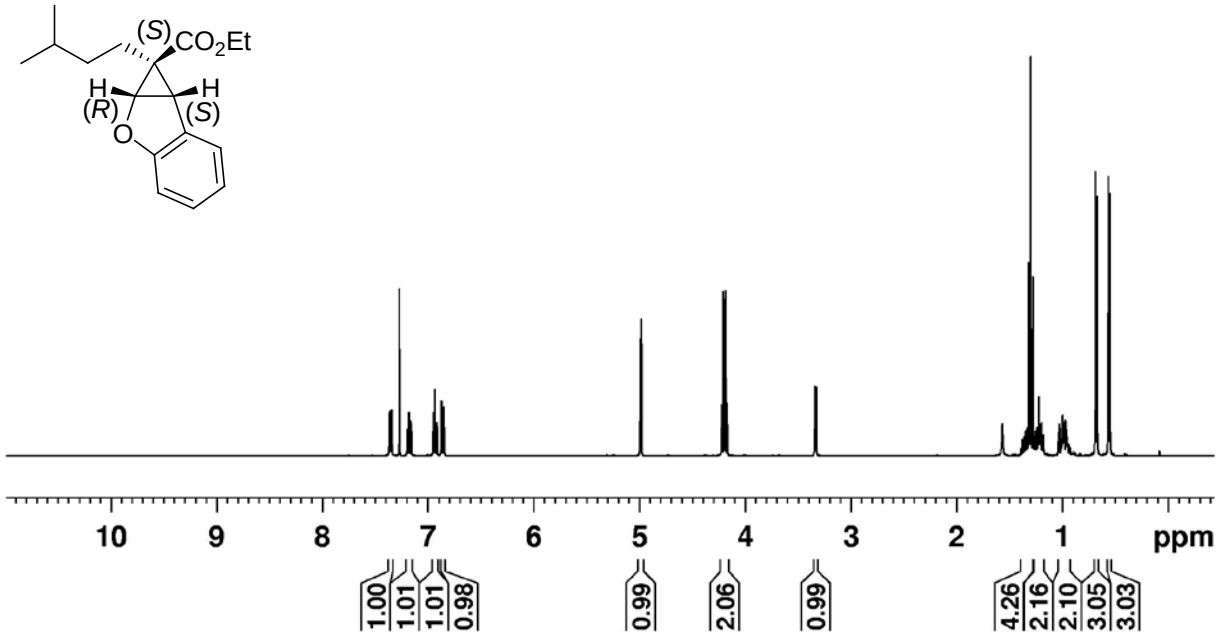
^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$)



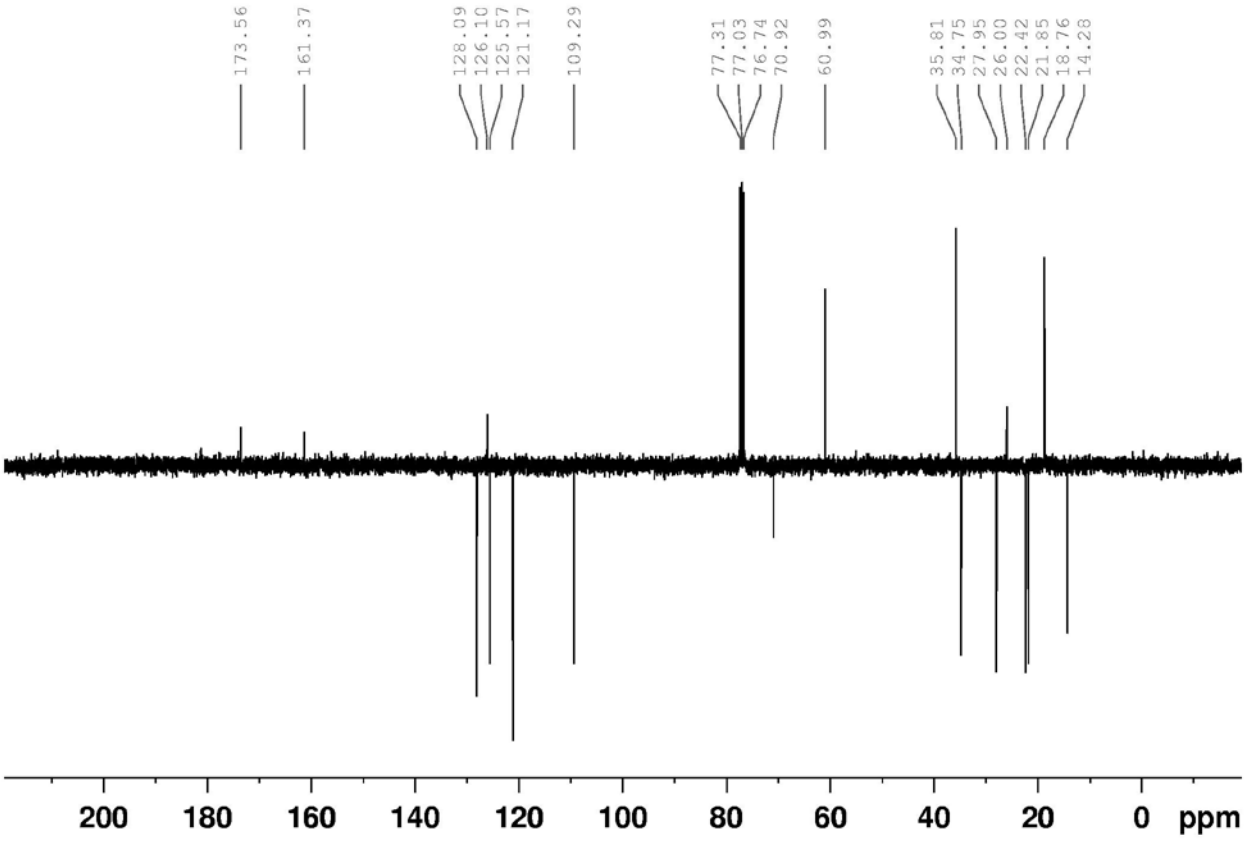
^{13}C NMR spectrum of **11** (100 MHz, $CDCl_3$)



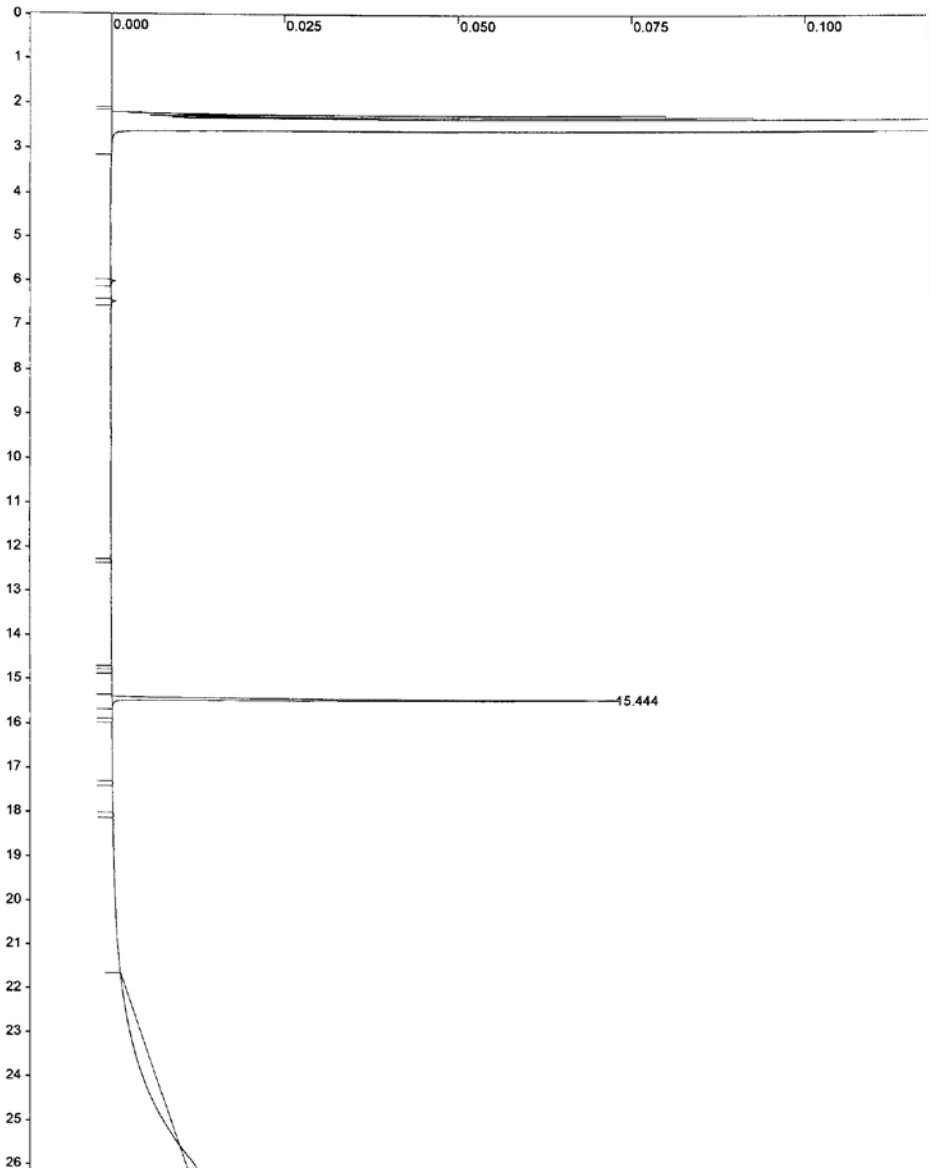
^{1}H NMR spectrum of **12** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **12** (100 MHz, $CDCl_3$)

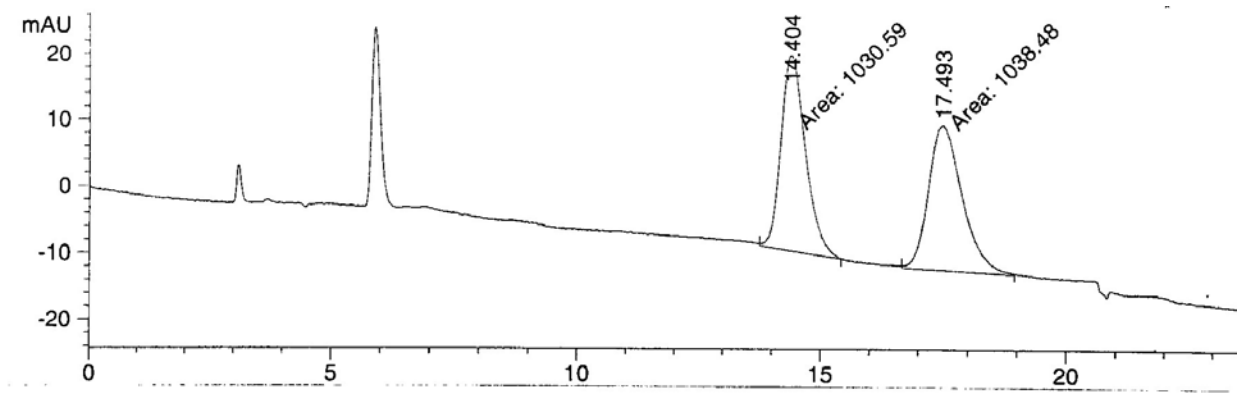


GC trace of **12** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)

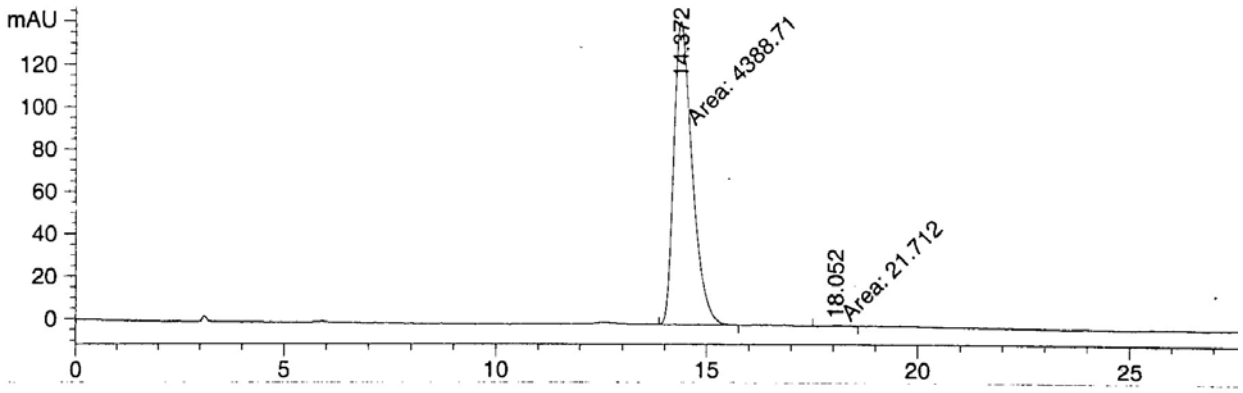


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	15.444	0.000	191507	BB	2.4	
Totals:		100.0000		0.000	191507			

HPLC resolution of racemic **12** (Chiracel OD column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)

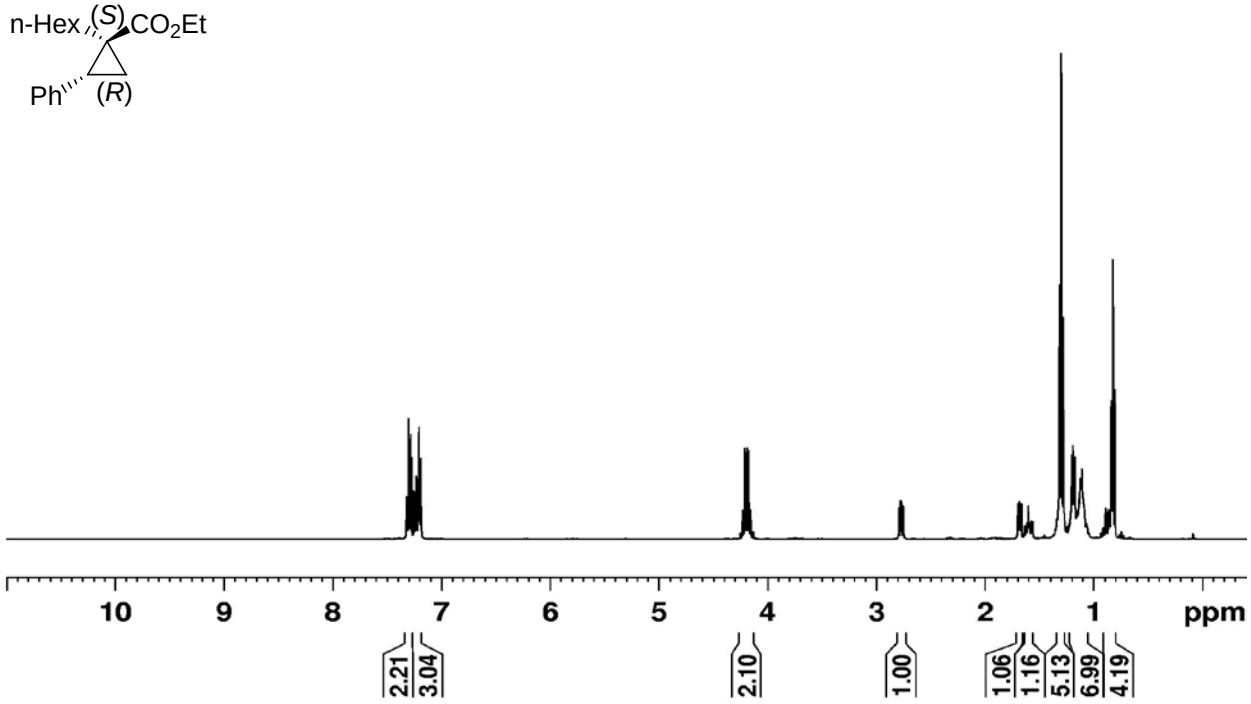


Enantiomeric excess of **12** (Chiracel OD column, 99.9:0.1 hexanes:isopropanol, 1 mL/min, 220 nm)

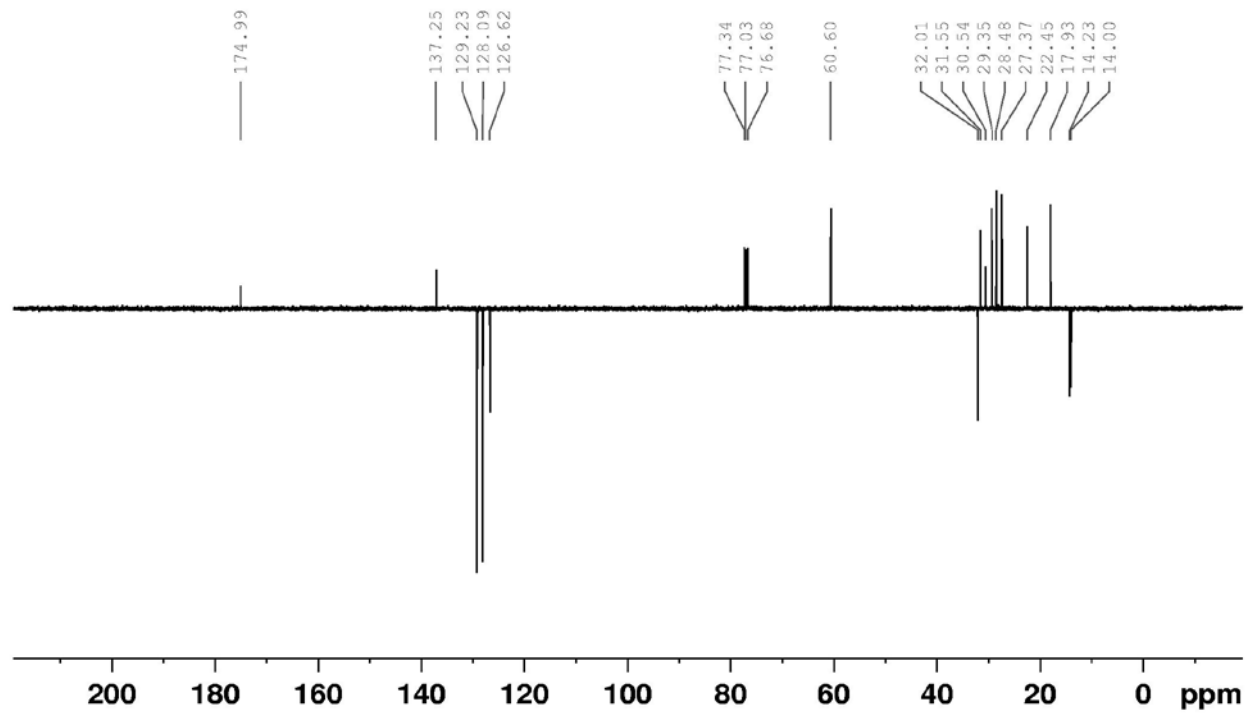


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.855	MM	0.6453	1.28008e4	330.62897	99.4258
2	22.678	MM	0.5099	73.92467	2.41642	0.5742
Totals :				1.28747e4	333.04539	

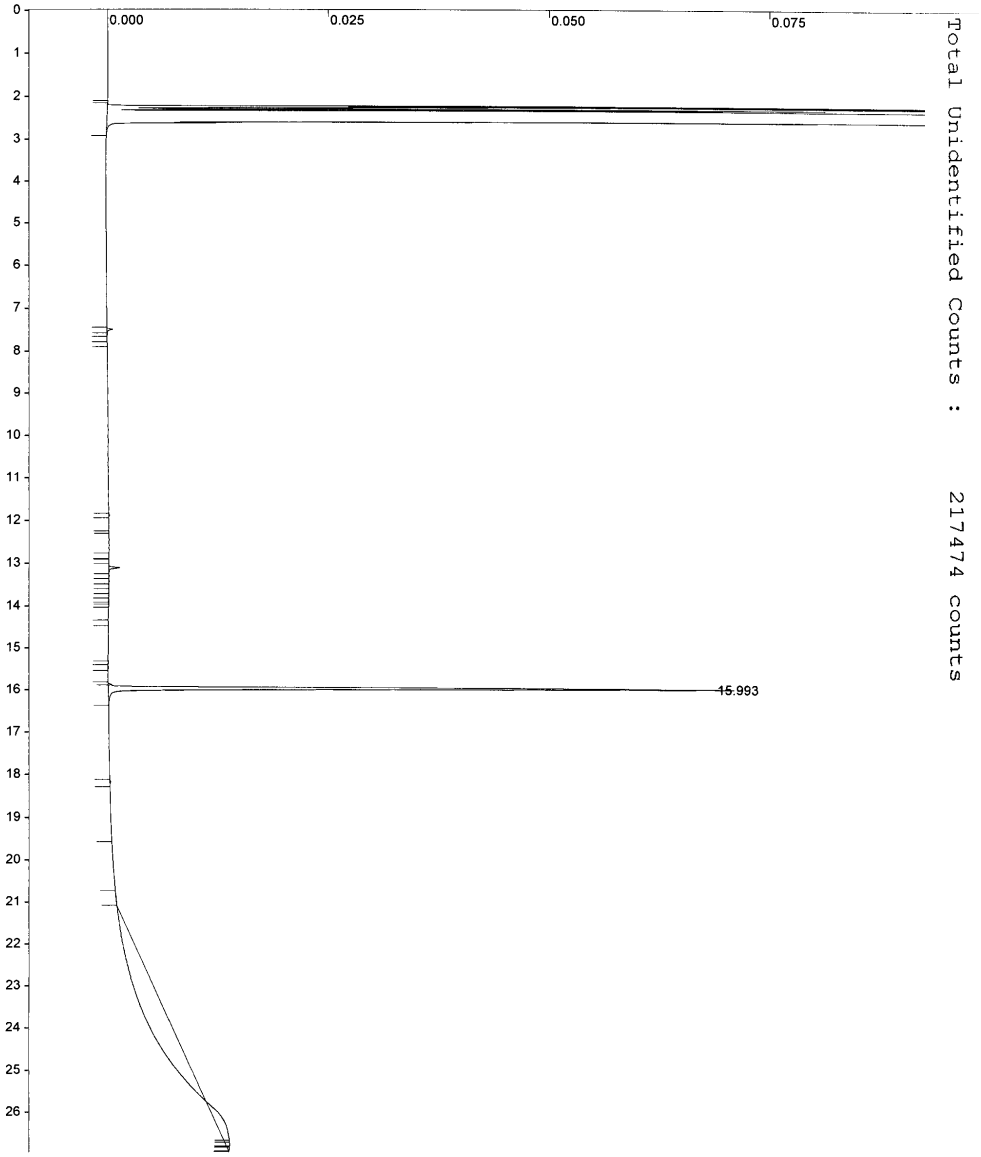
^{1}H NMR spectrum of **13** (400 MHz, $CDCl_3$)



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



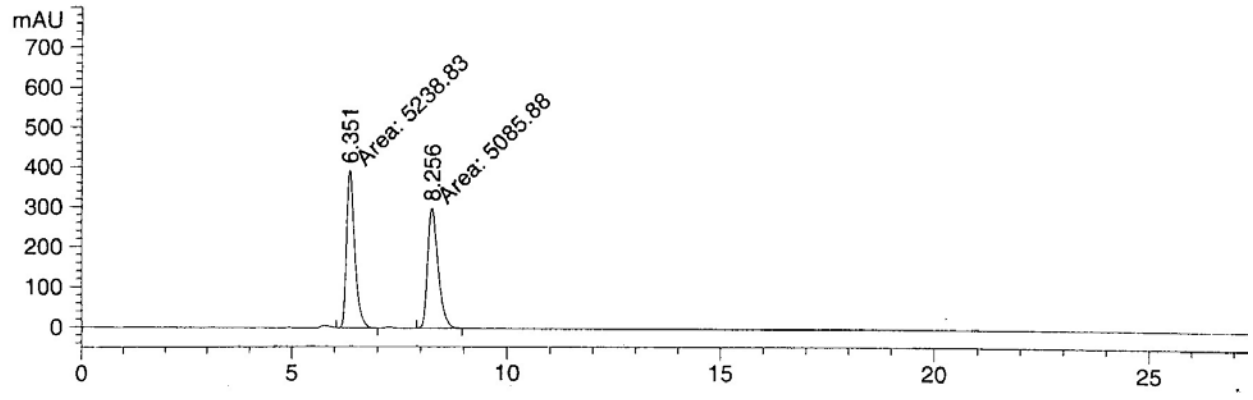
GC trace of **13** (Hewlett Packard HP1 column, 200 °C injection, 50–300 °C over 27 min)



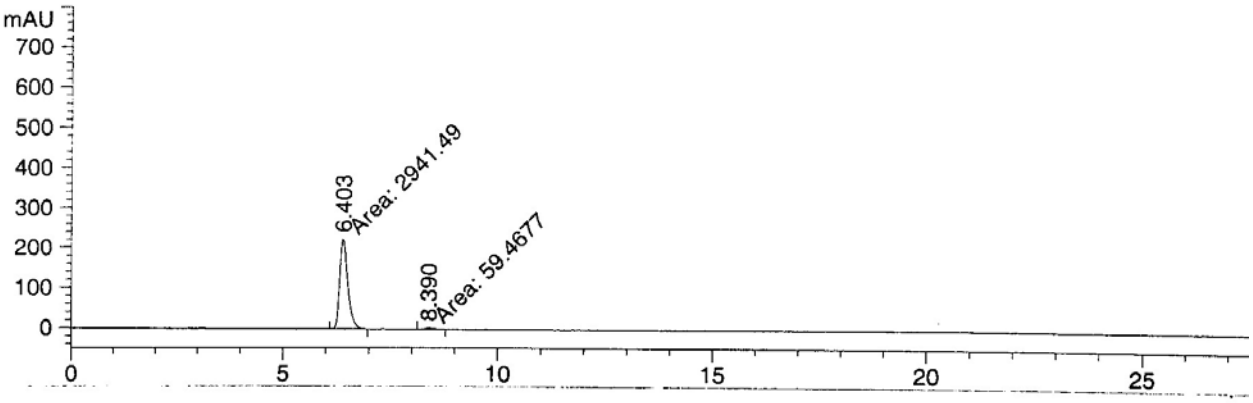
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		100.0000	15.993	0.000	217474	VB	2.8	
Totals:		100.0000		0.000	217474			

Total Unidentified Counts : 217474 counts

HPLC resolution of racemic **13** (Chiracel OD column, 99.8:0.2 hexanes:isopropanol, 1 mL/min, 220 nm)

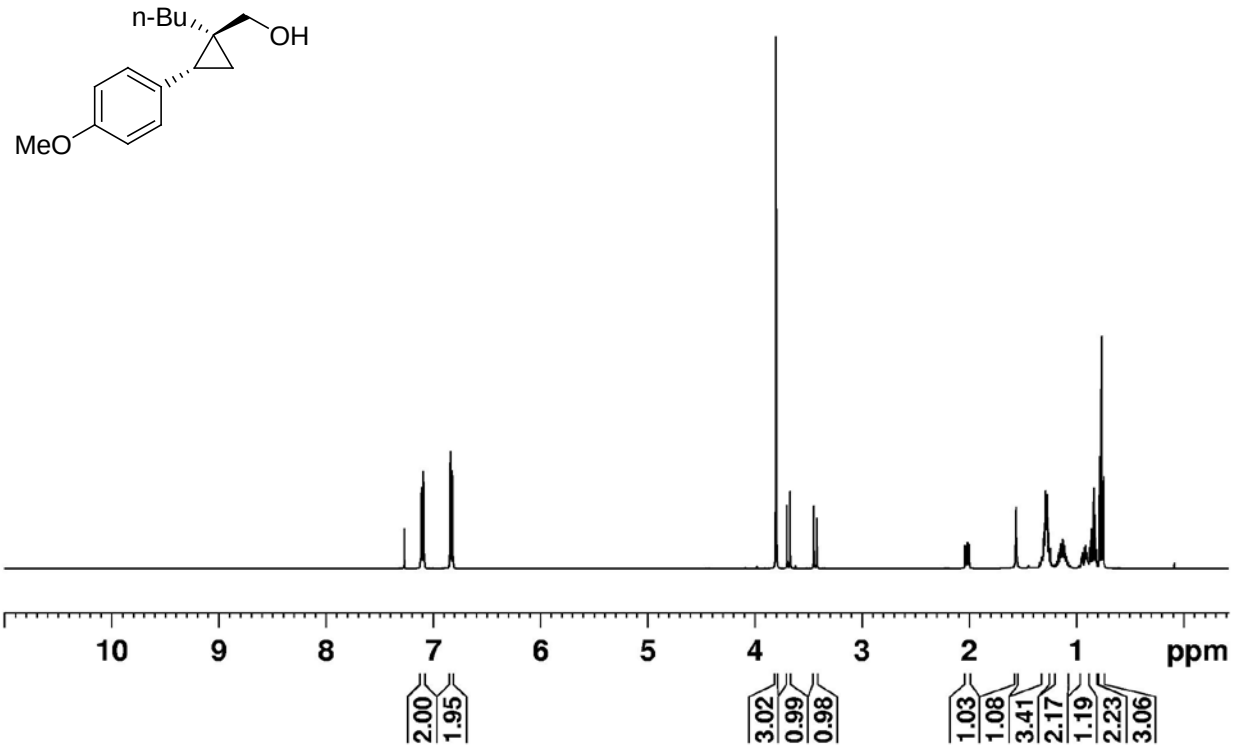


Enantiomeric excess of **13** (Chiracel OD column, 99.8:0.2 hexanes:isopropanol, 1 mL/min, 220 nm)

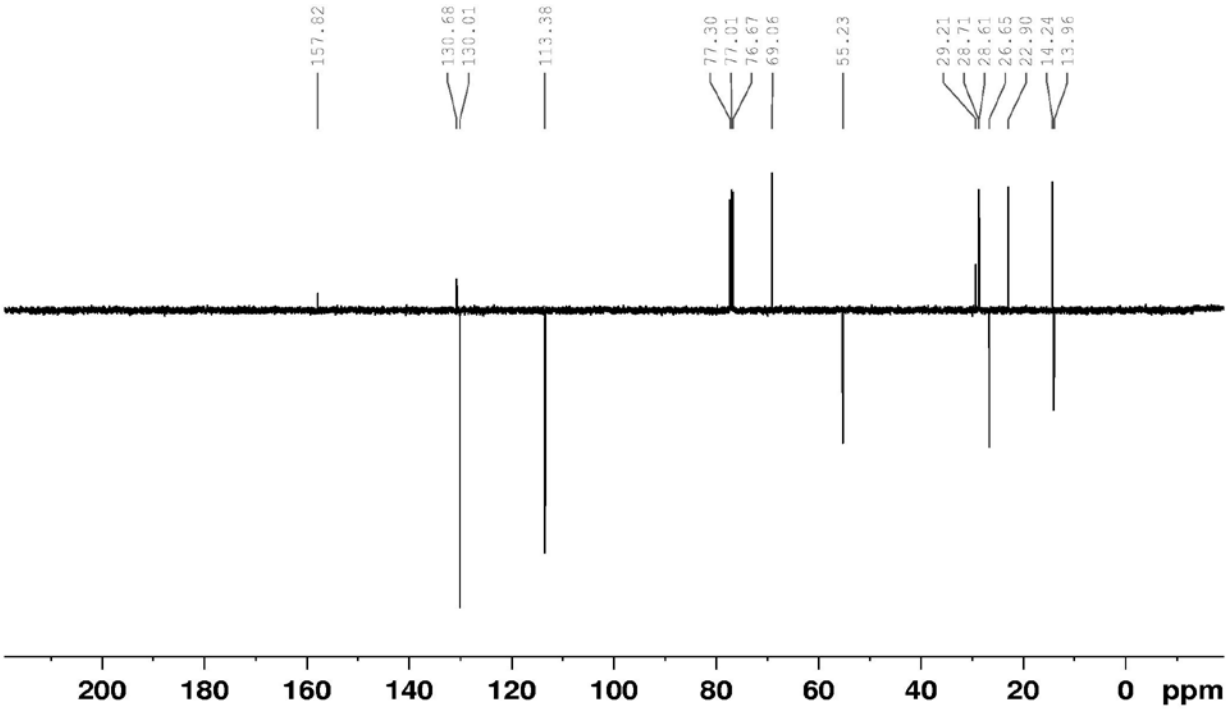


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.403	MM	0.2185	2941.48560	224.41888	98.0184
2	8.390	MM	0.2689	59.46766	3.68621	1.9816
Totals :				3000.95325	228.10509	

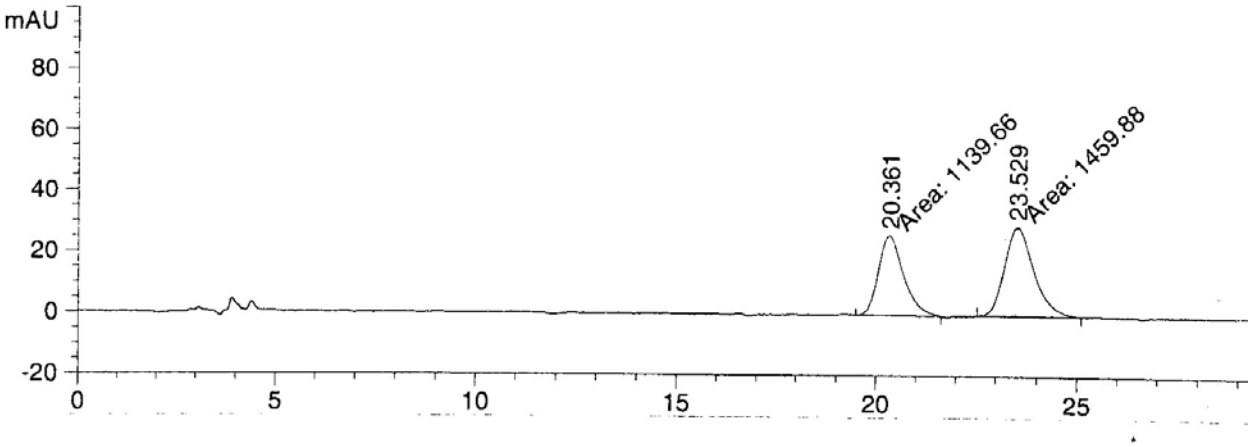
^{1}H NMR spectrum of **15** (400 MHz, $CDCl_3$)



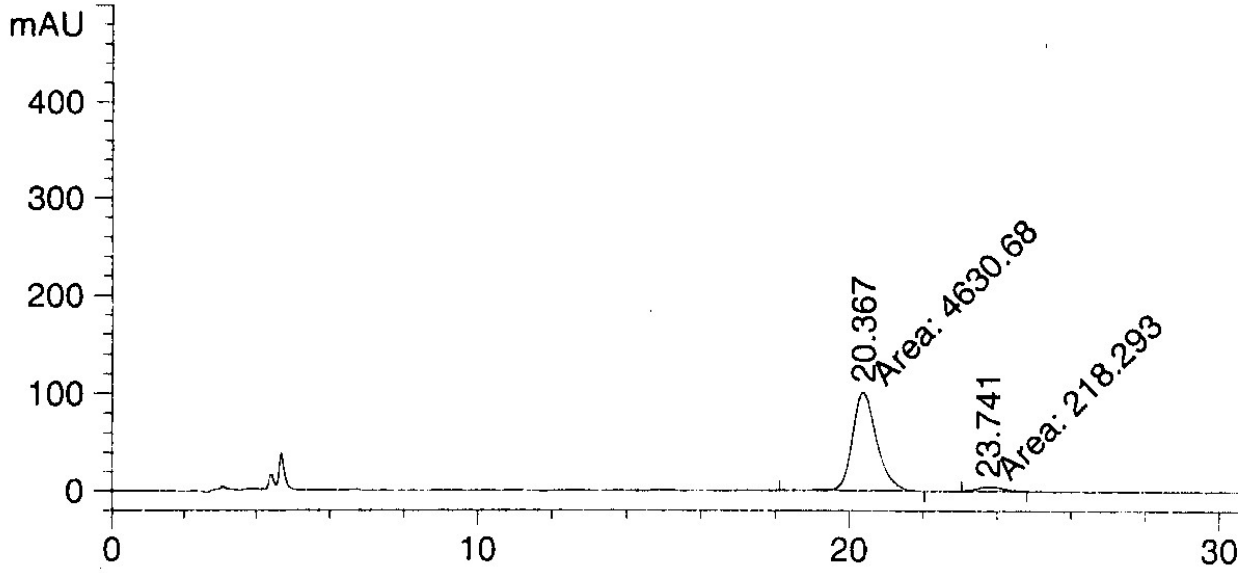
^{13}C NMR spectrum of **15** (100 MHz, $CDCl_3$)



HPLC resolution of **15** (Chiracel OD column, 98:2 hexanes: isopropanol, 1 mL/min, 220 nm)

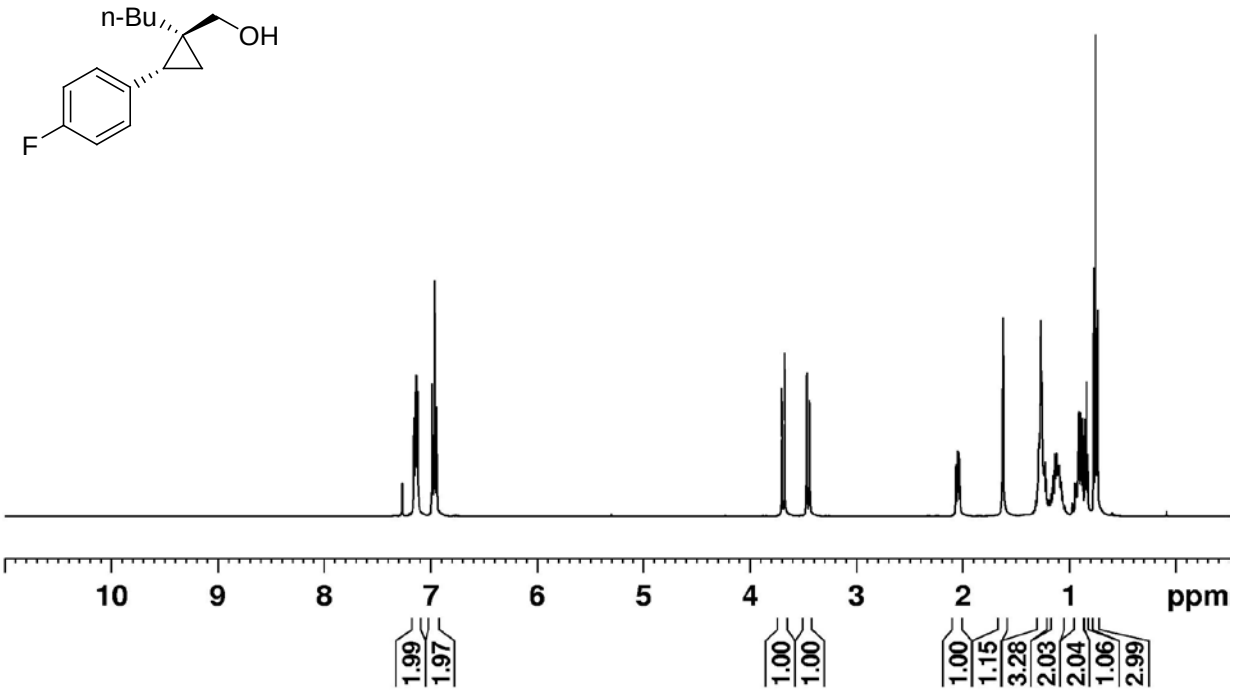


Enantiomeric excess of **15** (Chiracel OD column, 98:2 hexanes: isopropanol, 1 mL/min, 220 nm)

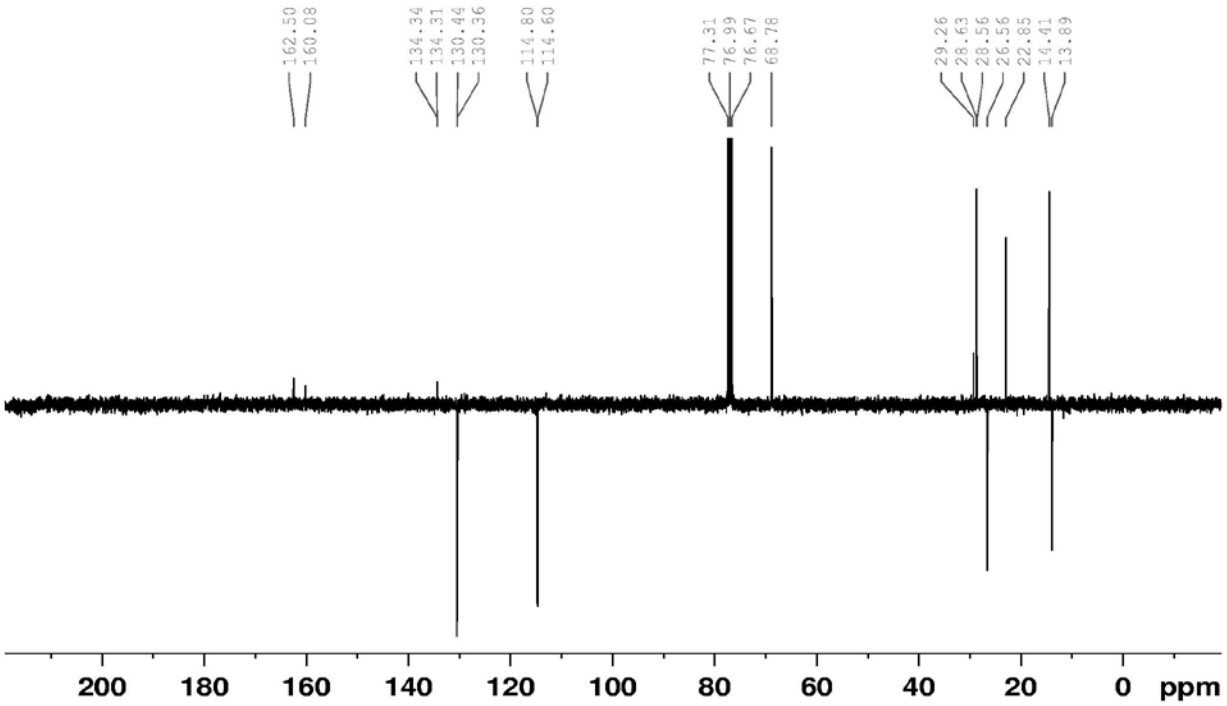


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.367	MM	0.7635	4630.68115	101.07853	95.4982
2	23.741	MM	0.7717	218.29338	4.71469	4.5018
Totals :				4848.97453	105.79322	

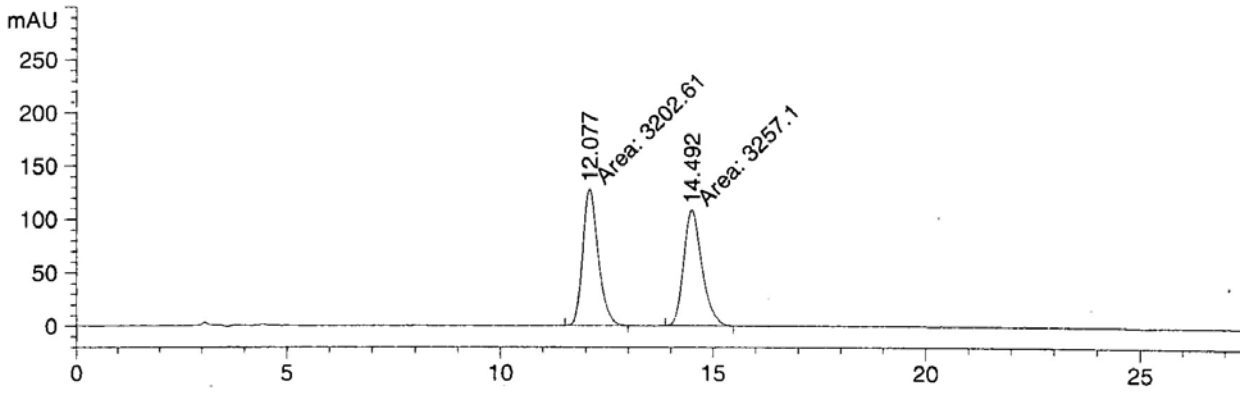
^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$)



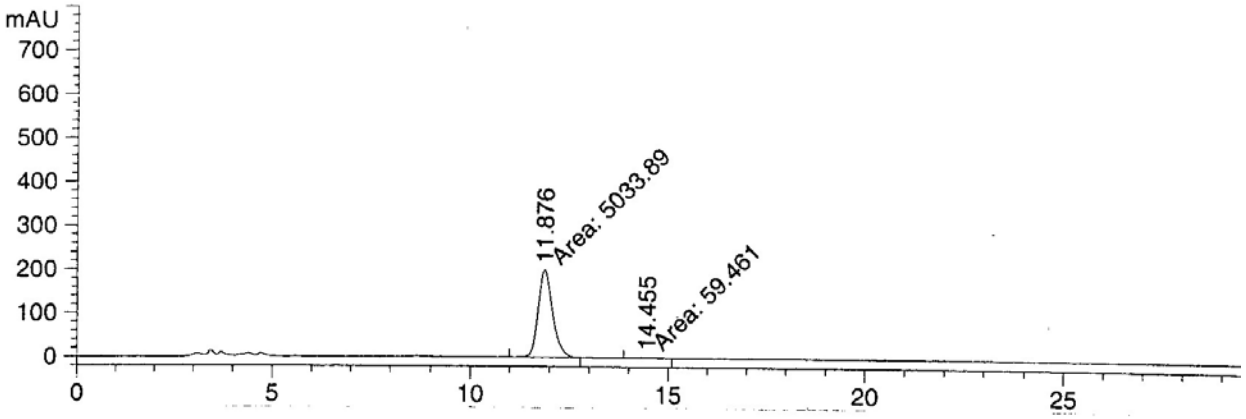
^{13}C NMR spectrum of **16** (100 MHz, $CDCl_3$)



HPLC resolution of **16** (Chiracel OD column, 98:2 hexanes: isopropanol, 1 mL/min, 220 nm)

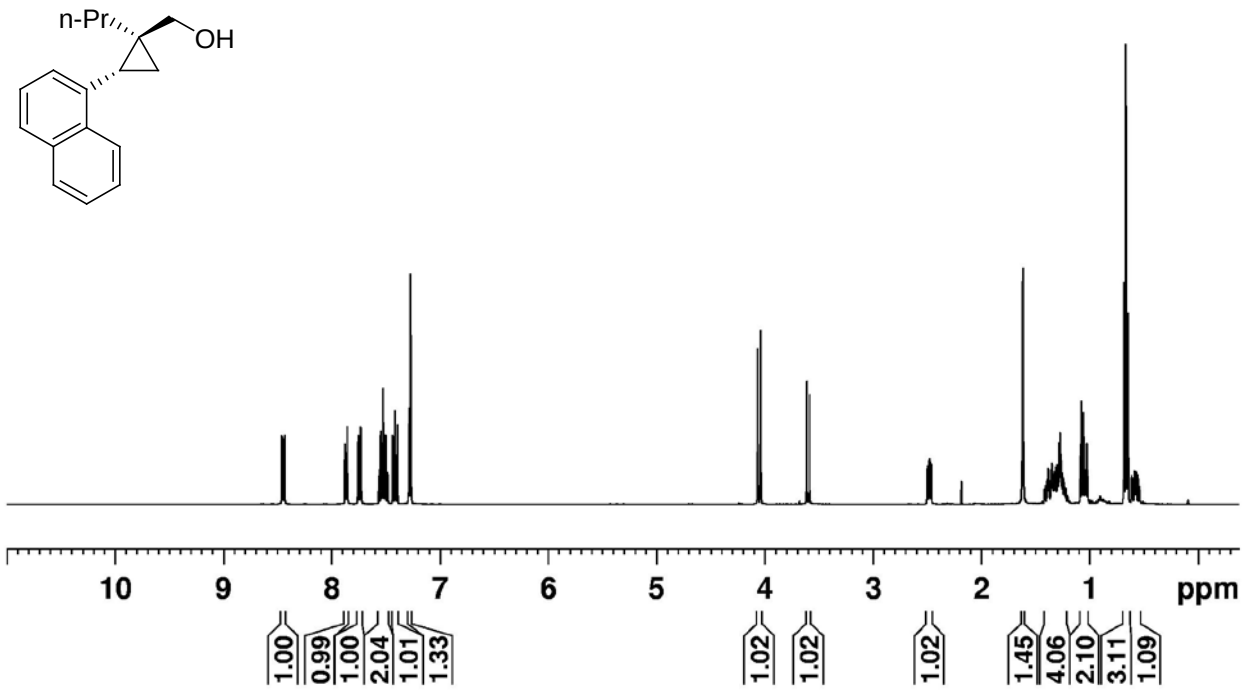


Enantiomeric excess of **16** (Chiracel OD column, 98:2 hexanes: isopropanol, 1 mL/min, 220 nm)

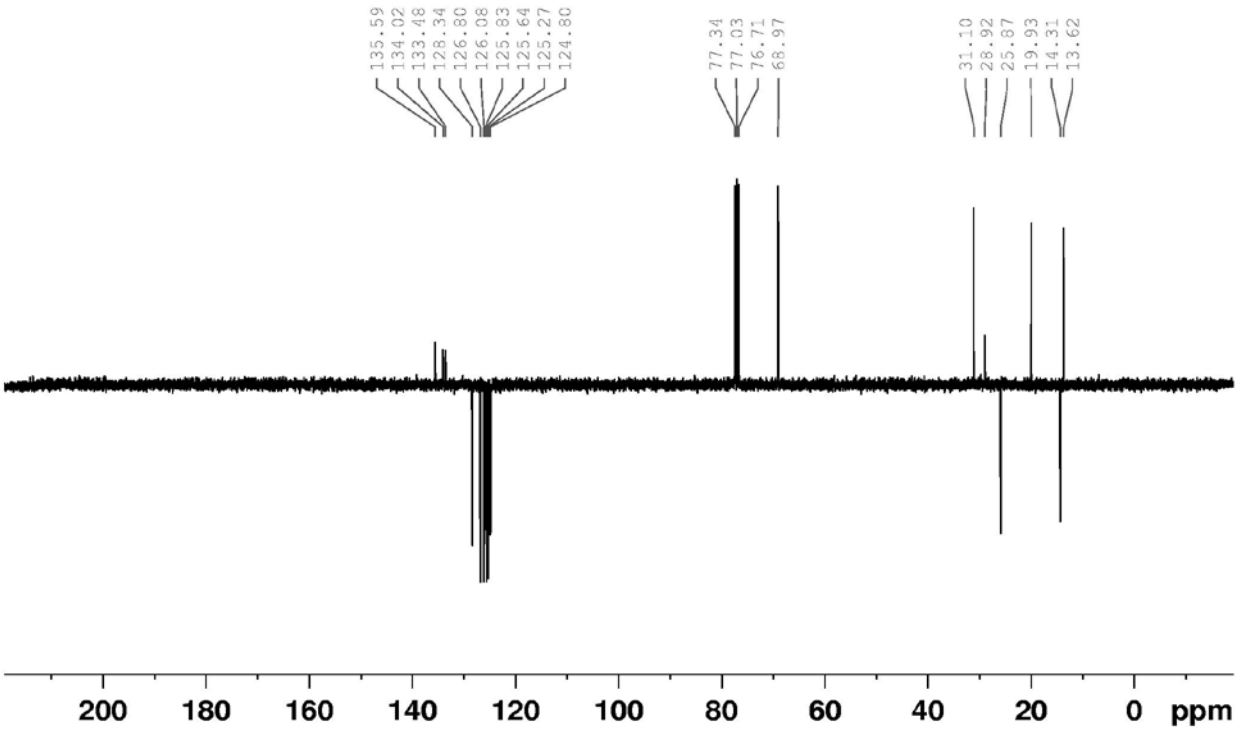


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.876	MM	0.4204	5033.89209	199.56914	98.8326
2	14.455	MM	0.4605	59.46101	2.15208	1.1674
Totals :				5093.35310	201.72121	

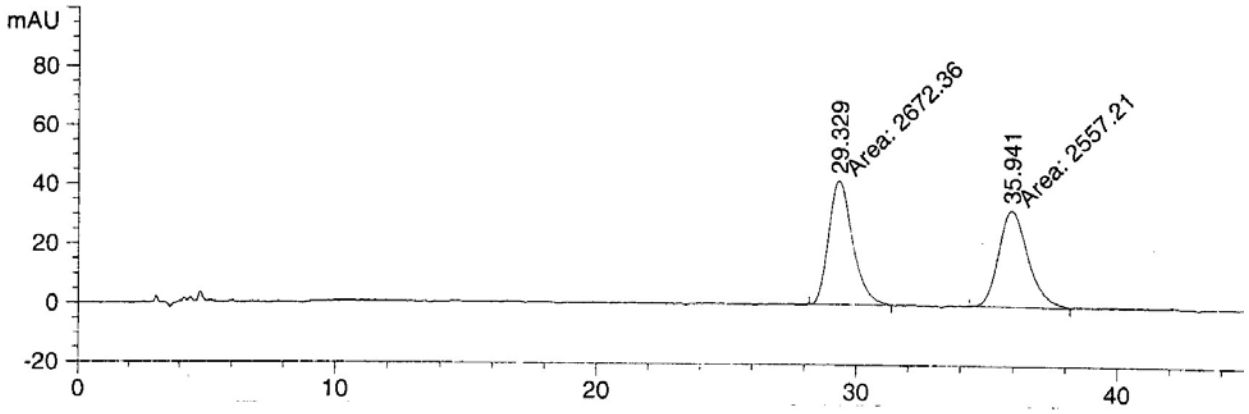
^{1}H NMR spectrum of **17** (400 MHz, $CDCl_3$)



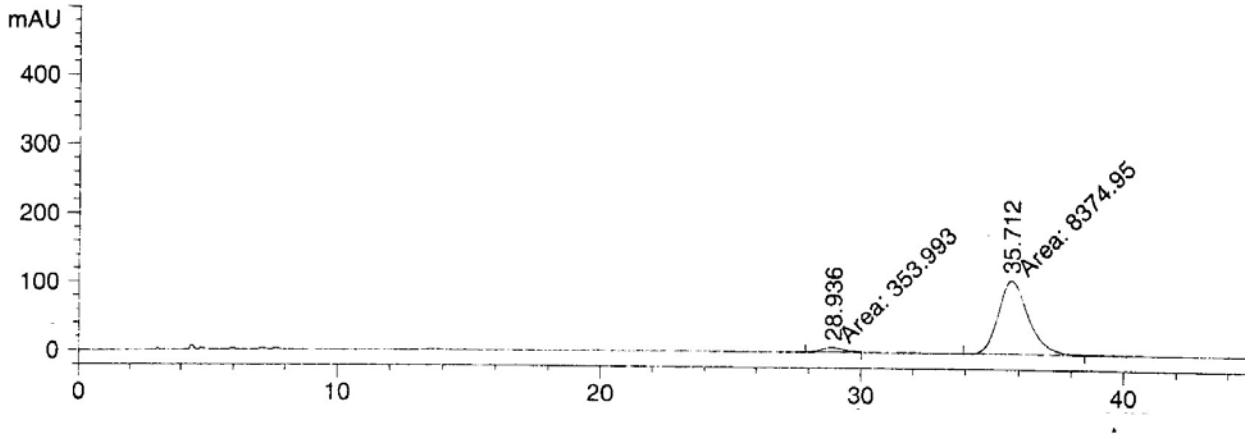
^{13}C NMR spectrum of **17** (100 MHz, $CDCl_3$)



HPLC resolution of **17** (Chiracel OD column, 98:2 hexanes:isopropanol, 1 mL/min, 220 nm)

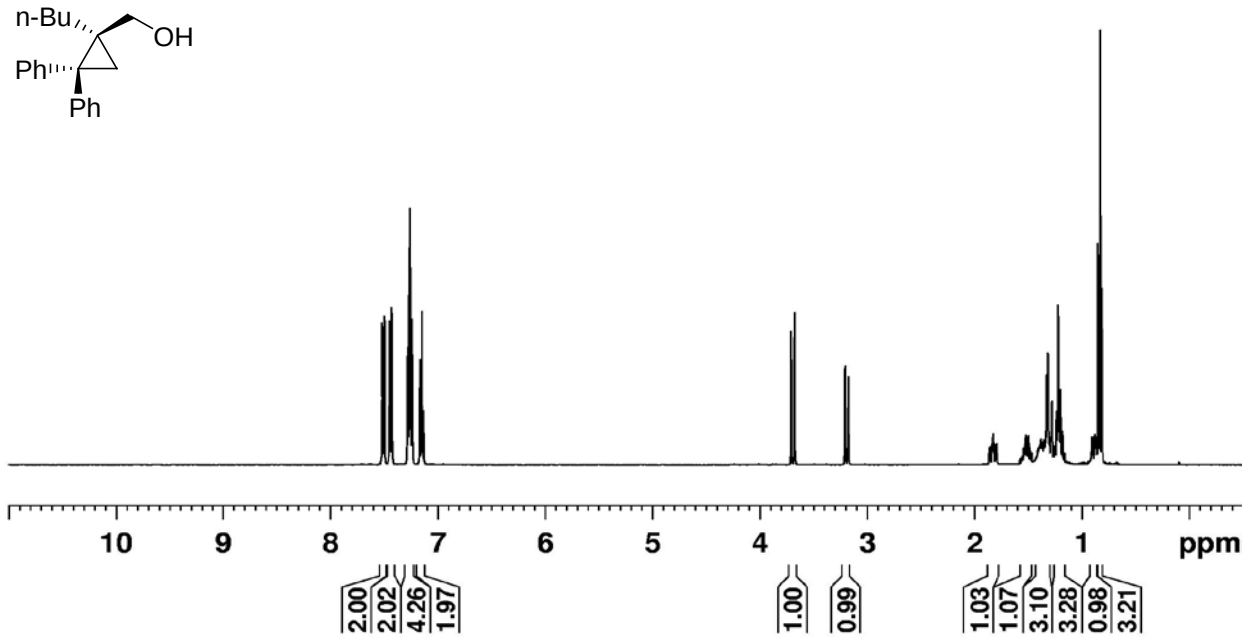


Enantiomeric excess of **17** (Chiracel OD column, 98:2 hexanes:isopropanol, 1 mL/min, 220 nm)

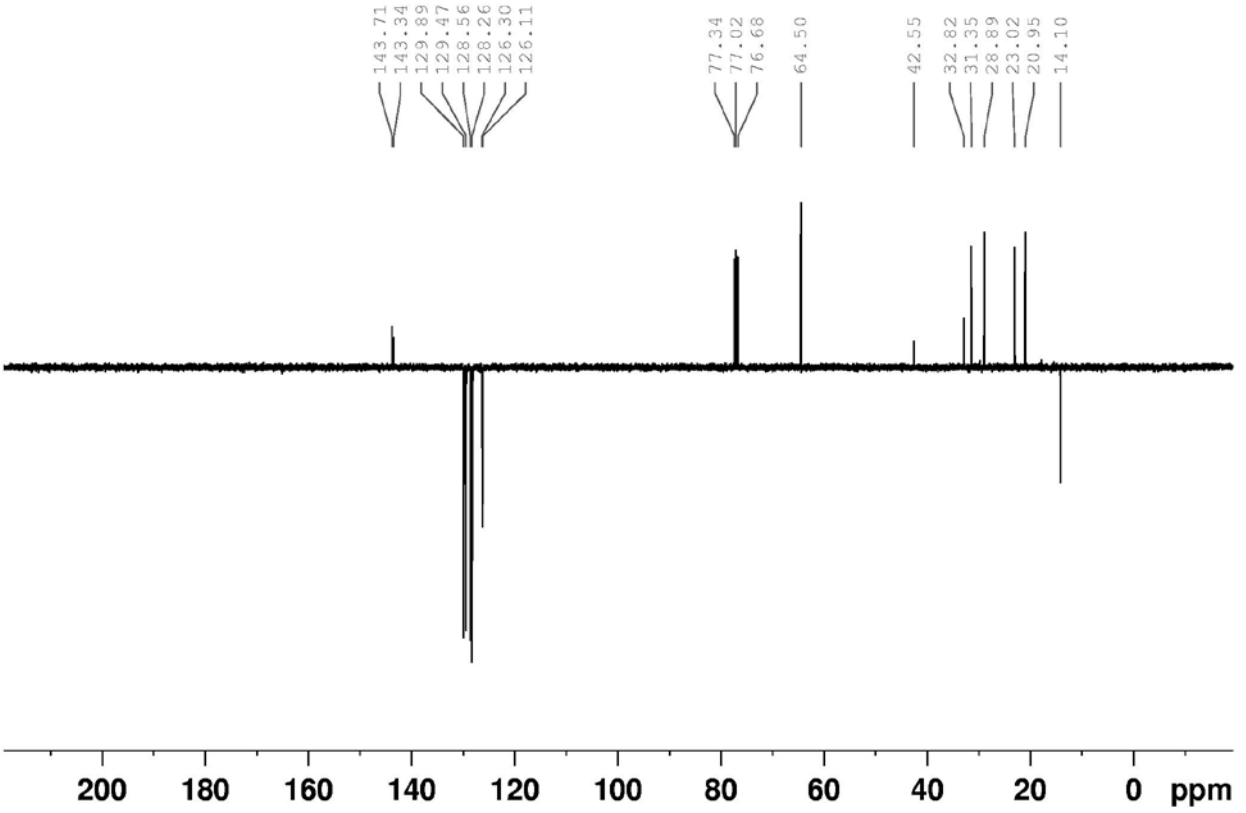


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.936	MM	0.9475	353.99332	6.22671	4.0554
2	35.712	MM	1.3106	8374.94531	106.50576	95.9446
Totals :				8728.93863	112.73247	

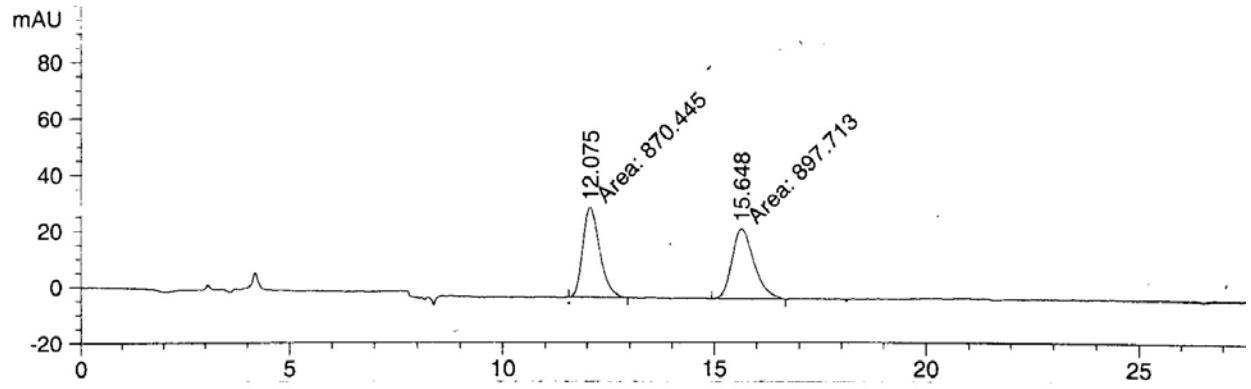
^{1}H NMR spectrum of **18** (400 MHz, $CDCl_3$)



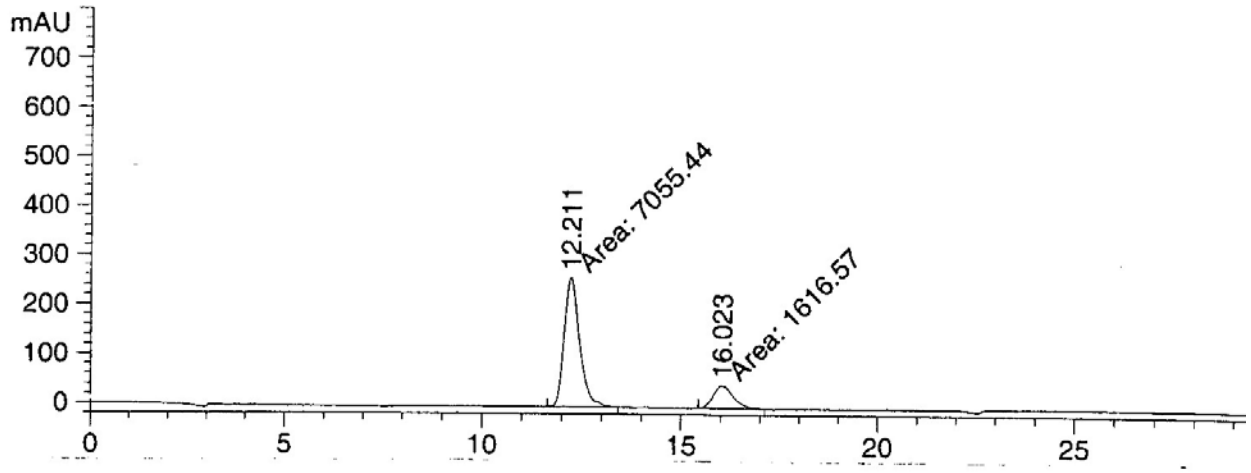
^{13}C NMR spectrum of **18** (100 MHz, $CDCl_3$)



HPLC resolution of racemic **18** (Chiracel OD column, 98:2 hexanes:isopropanol, 1 mL/min, 220 nm)

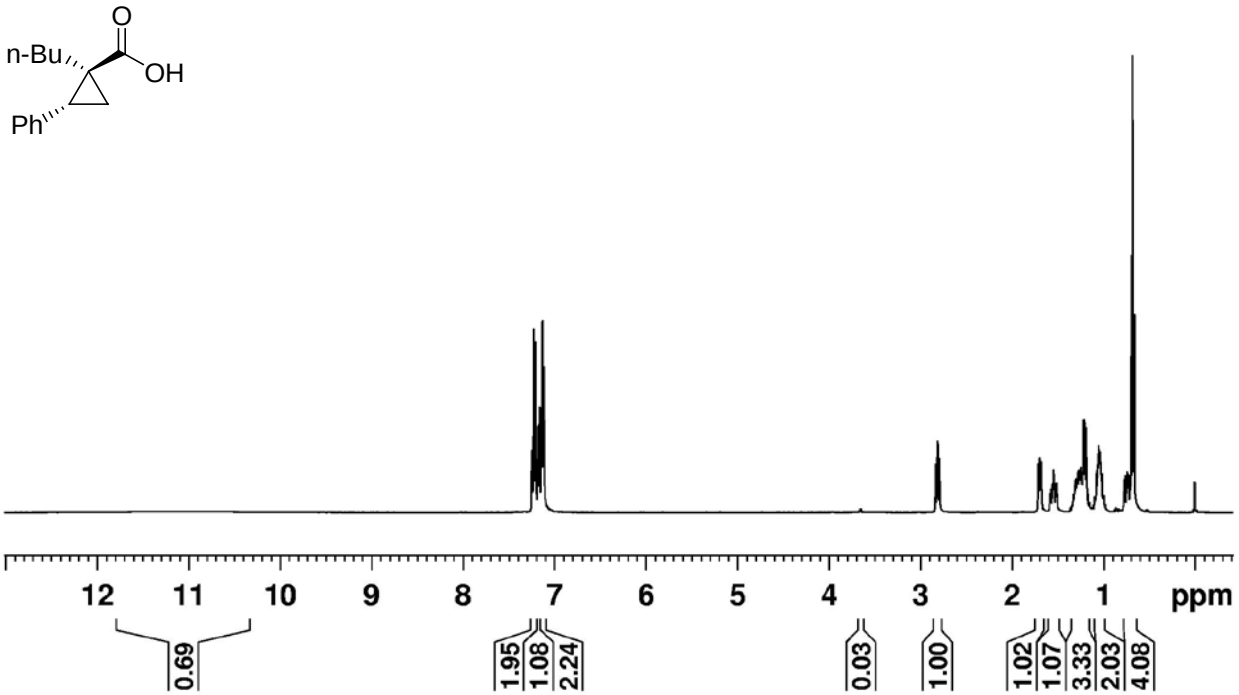


Enantiomeric excess of **18** (Chiracel OD column, 98:2 hexanes:isopropanol, 1 mL/min, 220 nm)

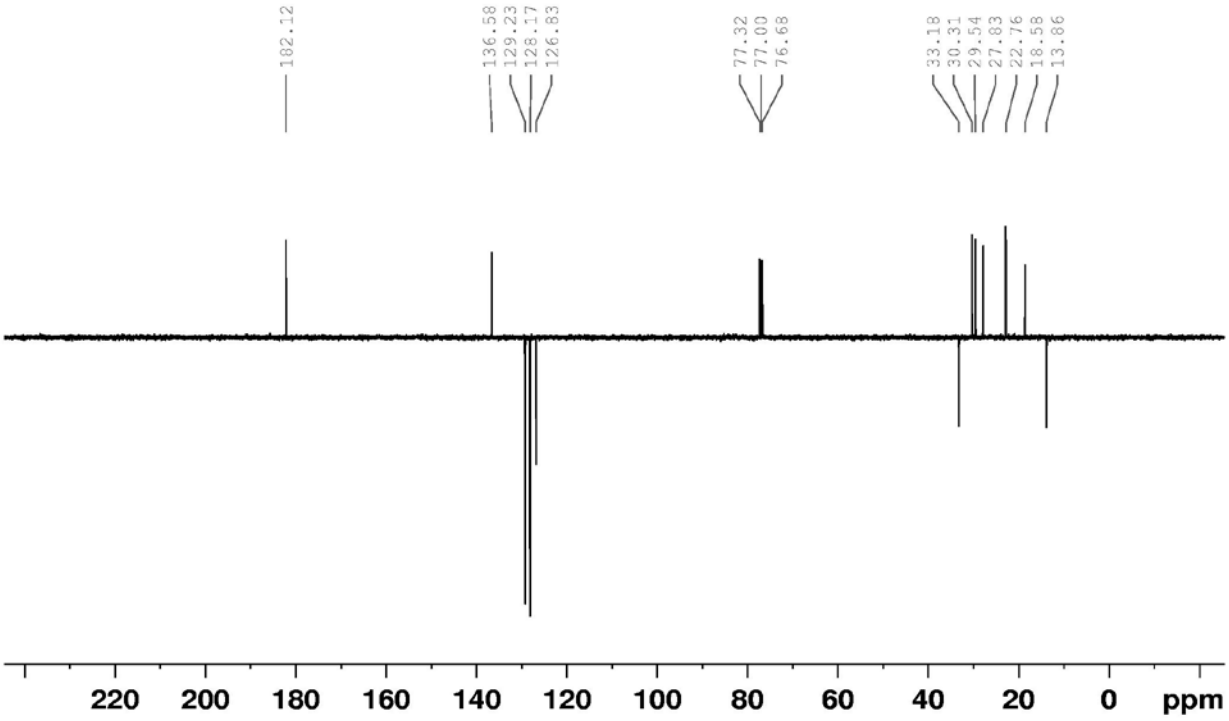


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.211	MM	0.4514	7055.43994	260.53018	81.3588
2	16.023	MM	0.5945	1616.56519	45.31838	18.6412
Totals :				8672.00513	305.84856	

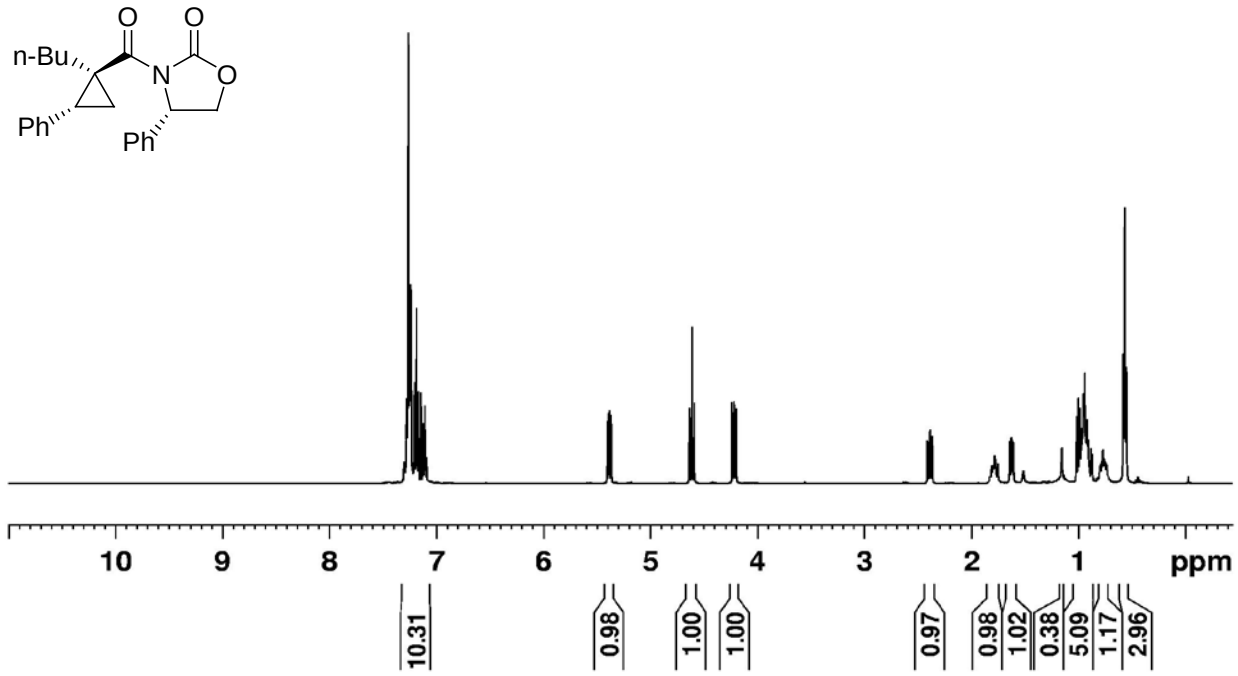
^{1}H NMR spectrum of **19** (400 MHz, $CDCl_3$) (97% purity)



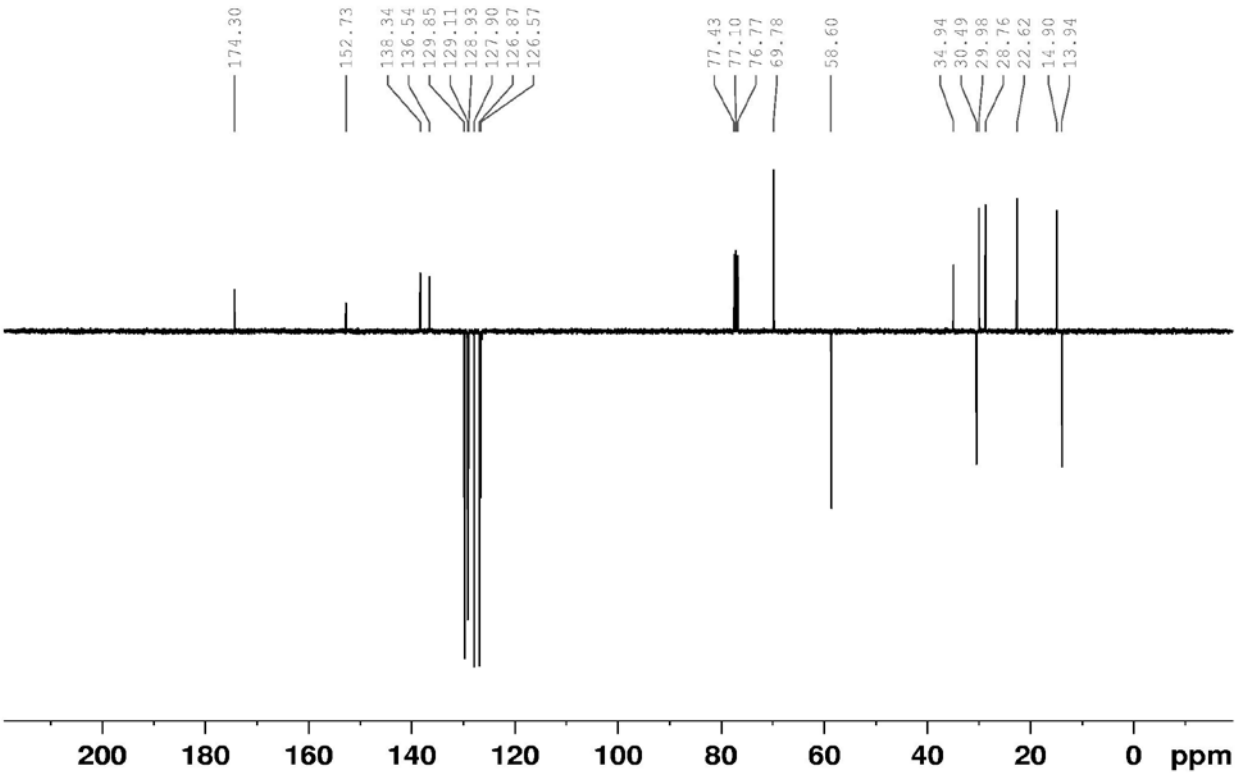
^{13}C NMR spectrum of **19** (100 MHz, $CDCl_3$) (97% purity)



^{1}H NMR spectrum of **20** (400 MHz, $CDCl_3$) (90% purity)



^{13}C NMR spectrum of **20** (100 MHz, $CDCl_3$) (90% purity)



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[2] Okamoto, T.; Kobayashi, K.; Oka, S.; Tanimoto, S. *J. Org. Chem*. **1988**, *53*, 4897.

[3] Hashimoto, S., Watanabe, N., Ikegami, S., *Tetrahedron Lett.* **1992**, 33, 2709.

[4] Tsutsui, H.; Abe, T.; Nakamura, S.; Anada, M.; Hashimoto, S. *Chem. Pharm. Bull.* **2005**, *10*, 1366-1368.

[5] Panne, P.; DeAngelis, A.; Fox, J. M. *Org. Lett.* **2008**, *10*, 2987