Electronic Supplementary Material (ESI) for Chemical Communications

Highly enantioselective ylide-mediated synthesis of terminal epoxides

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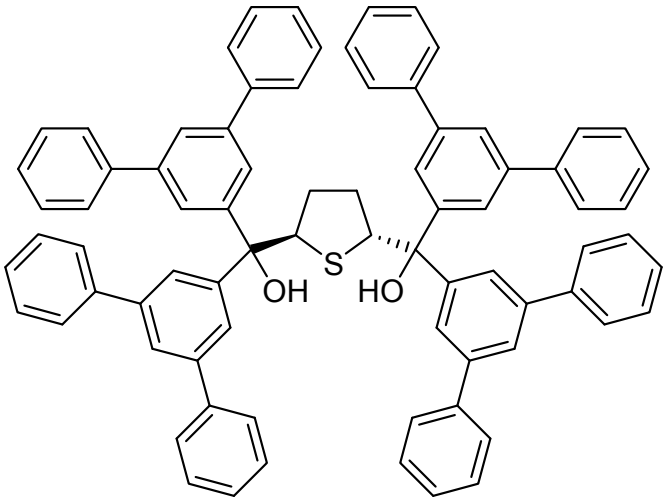
1.0 General

Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a universal ATR sampling accessory. Proton nuclear magnetic resonance (NMR) spectra were recorded on: Bruker Avance III 400 MHz, Bruker DPX400 400 MHz and Bruker Avance II 600 MHz spectrometers. ^{1}H NMR spectra were recorded at 400.23 MHz, 400.13 MHz and 600.13 MHz respectively. Chemical shifts are reported in ppm and coupling constants (*J*) are quoted in Hertz. ^{13}C NMR spectra were recorded on the previously mentioned instruments (100.64 MHz, 100.61 MHz & 150.9 MHz, respectively) with total proton decoupling. Fluorine NMR spectra were recorded on the Bruker DPX400 machine at 376.5 MHz). HSQC, HMBC, TOCSY and NOE NMR experiments were used to aid assignment of NMR peaks when required. Spectra recorded in $CDCl_3$ were referenced to residual $CHCl_3$ at 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C. A Waters micromass LCT-TOF mass spectrometer was used in ESI positive and ESI negative modes for electrospray ionization mass spectrometry. Chemical Ionization (CI) mass spectra were determined using a GCT-premier mass spectrometer in CI mode utilizing methane as the ionization gas. Electron Impact mass spectra were recorded on the same machine in EI mode. Flash chromatography was carried out using silica gel, particle size 0.04-0.063 mm and using a stepwise solvent polarity gradient correlated with TLC mobility. TLC analysis was performed on precoated $60F_{254}$ slides, and visualised by either UV irradiation or $KMnO_4$ staining. Specific rotation measurements were made on a Rudolph research analytical Autopol IV instrument, and are quoted in units of 10^{-1}degcm^2g^{-1}. All liquid aldehydes were freshly distilled at reduced prior to use, all solid aldehydes were recrystallised prior to use, unless otherwise stated, all chemicals were purchased from Aldrich and used as received. Anhydrous THF was distilled over sodium-benzophenone ketyl radical before use. All reactions were carried out under a protective argon atmosphere unless otherwise stated. Analytical CSP-HPLC was performed on Daicel CHIRALCEL OD-H (4.6 mm x 25 cm), OJ-H (4.6 mm x 25 cm), CHIRALPAK AD-H (4.6 mm x 25 cm) and AS (4.6 mm x 25 cm) columns. For all known compounds the spectral characteristics were in agreement with those reported in the literature.

2.0 Synthesis of catalyst 7f

2.1 (2*R*,5*R*)-Tetrahydro-2,5-[hydroxy-*bis*-(3,5-diphenylphenyl)methyl] thiophene



An oven dried round bottomed flask containing a stirring bar was charged with 3,5-diphenyl-1-bromobenzene[1] (2.16 g, 7.00 mmol), fitted with a septum and placed under an Ar atmosphere. Anhydrous THF (12.0 mL) was added *via* syringe and the solution was cooled to -20 °C. *t*BuLi (1.7 M solution in pentane, 4.11 mL, 7.00 mmol) was then added dropwise. After 20 minutes a solution of (2*R*,5*R*)-dimethyl tetrahydrothiophene-2,5-dicarboxylate (prepared from (2*R*,5*R*)-tetrahydrothiophene-2,5-dicarboxylic acid)[2] in THF (238 mg, 1.16 mmol, dissolved in 2.0 mL of THF) was added dropwise. The resulting solution was maintained at -20 °C for 1 h and then allowed to warm up to room temperature over 16 h. The solution was quenched with NH_4Cl (15 mL, saturated solution) and then extracted with Et_2O (4 x 20 mL). The combined organic extracts were dried over $MgSO_4$, evaporated under reduced pressure, and the crude product purified by column chromatography (hexane/CH_2Cl_2 1:1 *v*/*v*, R_f = 0.25) affording (2*R*,5*R*)-tetrahydro-2,5-[hydroxy-*bis*-(3,5-diphenylphenyl)methyl]thiophene as a white solid (880 mg, 71%). M.p. 259-261 ^oC. $[\alpha]_D^{20}$ +190 (*c* 0.34, CH_2Cl_2).

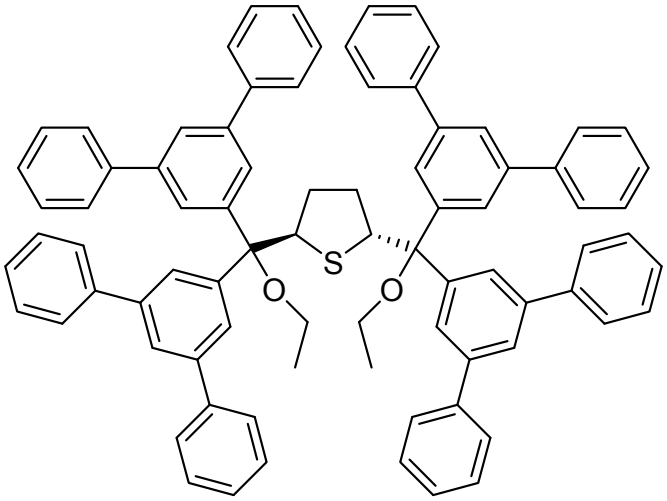
^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 4H), 7.77 (s, 4H), 7.66 (s, 4H), 7.65-7.60 (m, 16H), 7.48-7.43 (m, 16H), 7.39-7.27 (m, 8H), 5.04-4.98 (m, 2H), 3.77 (bs, 2H), 2.17-2.12 (m, 2H), 1.87-1.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 145.3, 141.8, 141.6, 141.13, 141.10, 128.7 (x2), 127.44, 127.41, 127.3 (x2), 125.5, 124.7, 123.9, 123.2, 77.7, 60.9, 31.9.

IR ν_{max}: 3490, 3050, 2956, 1595, 1500, 1308, 1199, 1112, 1017, 937.

HRMS (MALDI): calcd. for $[M+Na]^+$ $C_{78}H_{60}O_2NaS$ requires 1083.4212, found 1083.4243.

2.2 (2*R*,5*R*)-Tetrahydro-2,5-[ethoxy-*bis*-(3,5-diphenylphenyl)methyl]thiophene



An oven dried round bottomed flask containing a stirring bar was charged with (2*R*,5*R*)-Tetrahydro-2,5-[hydroxy-*bis*-(3,5-diphenylphenyl)methyl]thiophene (100 mg, 0.09 mmol), fitted with a septum and placed under an Ar atmosphere. Anhydrous THF (1.0 mL) and anhydrous DMF (0.25 mL) were added sequentially *via* syringe and the solution was cooled to 0 °C. NaH (60% in mineral oil, 22 mg, 0.54 mmol) was added and the resulting solution was allowed to stir for 10 minutes at 0 °C. Iodoethane (145 µL, 1.80 mmol) was injected *via* syringe. The solution was allowed to slowly warm up to room temperature. After 16 h water (10 mL) was carefully added with stirring. After 10 minutes CH_2Cl_2 (10 mL) was added to the solution. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$ and then evaporated under reduced pressure. The crude material was purified by column chromatography (hexane/CH_2Cl_2 7:3 *v*/*v*, R_f = 0.3) affording (2*R*,5*R*)-tetrahydro-2,5-[ethoxy-*bis*-(3,5-diphenylphenyl)methyl]thiophene as a white solid (89 mg, 85%). M.p. 90-92 °C. $[\alpha]_D^{20}$ +87 (*c* 0.9, CH_2Cl_2).

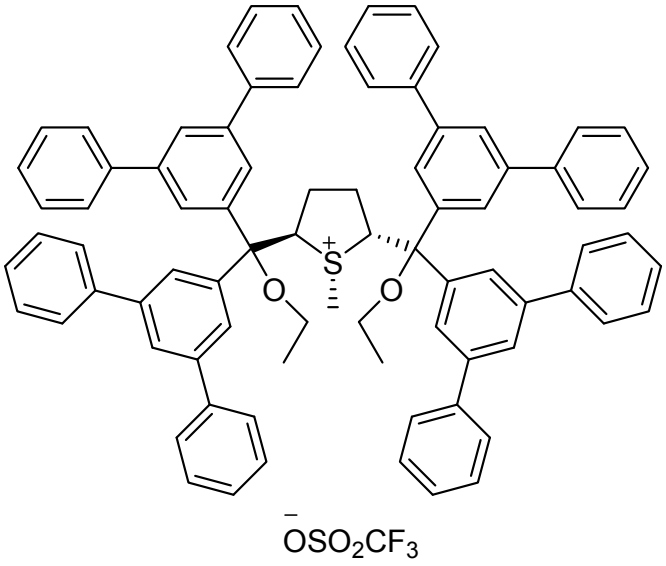
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 8H), 7.72 (s, 4H), 7.69-7.62 (m, 16H), 7.51-7.32 (m, 24H), 4.49-4.32 (m, 2H), 3.51-3.39 (m, 2H), 3.30-3.18 (m, 2H), 2.00-1.86 (m, 4H), 1.16 (t, J = 7.3 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 142.4, 140.8, 140.7, 140.2, 140.0, 128.4, 128.3, 126.8 (x2), 126.78 (x2), 126.71, 126.6, 124.7, 124.6, 85.2, 58.9, 54.5, 31.2, 15.4.

IR ν_{max}: 3060, 3034, 2924, 2854, 1721, 1594, 1496, 1453, 1062, 875, 755, 694.

HRMS (MALDI): calcd. for $[M+Na]^+$ $C_{82}H_{68}O_2NaS$ requires 1139.4838, found 1139.4845.

2.3 (2*R*,5*R*)-Tetrahydro-2,5-[ethoxy-*bis*-(3,5-diphenylphenyl)methyl] thiophene methyl sulfonium triflate salt (7f)



An oven dried round bottomed flask containing a stirring bar was charged with (2*R*,5*R*)-tetrahydro-2,5-[ethoxy-*bis*-(3,5-diphenylphenyl)methyl]thiophene (90 mg, 0.08 mmol) and proton sponge (8 mg, 0.04 mmol), fitted with a septum and placed under an Ar atmosphere. Anhydrous CH_2Cl_2 (0.8 mL) was added *via* syringe. Methyl triflate (9 µL, 0.08 mmol) was then added to the solution *via* syringe. The resulting solution was allowed to stir at room temperature for 16 h. The solution was then evaporated under reduced pressure and the crude material was directly purified by column chromatography (hexane/ethyl acetate 7:3 *v*/*v*, R_f = 0.15) affording **7f** as a white solid (46 mg, 45%). The unreacted sulfide can be effectively recovered from the column chromatography (early eluting spot). M.p. 161-162 ^{o}C. $[\alpha]_D^{20}$ +143 (*c* 0.55, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.81 (s, 1H), 7.75 (bs, 2H), 7.70-7.58 (m, 8H), 7.57-7.53 (m, 6H), 7.49-7.21 (m, 34H), 6.01-5.92 (m, 1H), 3.75-3.60 (m, 1H), 3.45-3.33 (m, 2H), 3.32-3.24 (m, 3H), 3.19-3.08 (m, 1H), 3.06 (s, 3H), 2.70-2.61 (m, 1H), 2.36-2.27 (m, 1H), 1.23-1.16 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 142.3, 142.27, 142.22, 141.8, 141.3, 140.2, 140.0, 139.95, 139.90, 139.2, 138.4, 128.98 (x5), 128.94, 127.99, 127.94, 127.8, 127.3, 127.2, 127.1, 127.0, 126.9, 126.8, 126.7, 126.6, 125.7, 124.1, 121.8, 85.2, 83.6, 72.9, 69.7, 62.1, 60.7, 30.6, 30.1, 23.1, 15.3, 15.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -78.5.

IR ν_{max}: 3070, 2960, 2941, 2822, 1711, 1597, 1500, 1350, 1257, 1159, 1021, 866, 757.

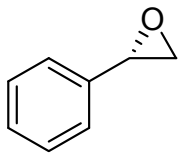
HRMS (MALDI): calcd. for $[M]^+$ $C_{83}H_{71}O_2S$ requires 1131.5175, found 1131.5194.

3.0 General procedure A for the enantioselective epoxidation of aldehydes using catalyst 7f

An oven dried round bottomed flask containing a stirring bar was charged with **7f** (1.0 eq.), fitted with a septum and placed under an Ar atmosphere. Anhydrous THF was added *via* syringe, followed by the relevant aldehyde (1.0 eq.). The solution was cooled to -78 °C. Phosphazene base P_2-*t*Bu (2 M in THF, 1.0 eq.) was added *via* syringe and the resulting solution was maintained at -78 °C for 1 h, then allowed to slowly warm up to room temperature. The solution was then partitioned between CH_2Cl_2 (10 mL) and water (10 mL) and the two phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$, evaporated under reduced pressure and the crude material purified by column chromatography.

4.0 Characterization data for the epoxide products (Table 2)

4.1 (*S*)-2-phenyloxirane [(*S*)-2]



Prepared according to general procedure A using **1** (26 µL, 0.26 mmol), **(*R*,*R*)-7f** (333 mg, 0.26 mmol), P_2-*t*Bu base (130 µL) and THF (13.0 mL). Column chromatography

(hexane/CH_2Cl_2 8:2 *v*/*v*, R_f = 0.2) afforded **(*S*)-2** as a colourless oil (29.6 mg, 95%). $[\alpha]_D^{20}$ +20 (*c* 1, $CHCl_3$); lit.[3] $[\alpha]_D^{20}$ -24 (*c* 1, $CHCl_3$, *ent*).

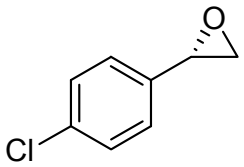
The NMR spectra of **(*S*)-2** were consistent with those previously reported:[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.12 (m, 5H), 3.88 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.16 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.82 (dd, *J* = 5.5, 2.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2, 128.1, 127.7, 125.1, 51.9, 50.8.

HRMS (ESI): calcd. for $[M+H]^+$ C_8H_9O requires 121.0653, found 121.0659.

4.2 (*S*)-*2*-(4-chlorophenyl)oxirane [(*S*)-16]



Prepared according to general procedure A using **8** (30 mg, 0.22 mmol), **(*R*,*R*)-7f** (281 mg, 0.22 mmol), P_2-*t*Bu base (110 µL) and THF (11.0 mL). Column chromatography (hexane/CH_2Cl_2 1:1 *v*/*v*, R_f = 0.3) afforded **(*S*)-16** as a colourless oil (31.2 mg, 92%). $[\alpha]_D^{20}$ +23 (*c* 0.3, $CHCl_3$); lit.[4] $[\alpha]_D^{20}$ +25 (*c* 1.0, $CHCl_3$).

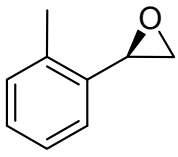
The NMR spectra of **(*S*)-16** were consistent with those previously reported:[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 3.84 (dd, *J* = 4.0, 2.5 Hz, 1H), 3.15 (dd, *J* = 5.5, 4.0 Hz, 1H), 2.76 (dd, *J* = 5.5, 2.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.1, 133.9, 128.7, 126.8, 51.8, 51.2.

HRMS (EI): calcd. for $[M]^+$ C_8H_7OCl requires 154.0185, found 154.0182.

4.3 (*R*)-2-(2-tolyl)oxirane [(*R*)-17]



Prepared according to general procedure A using **9** (22 µL, 0.20 mmol), **(*S*,*S*)-7f** (256 mg, 0.20 mmol), P_2-*t*Bu base (100 µL) and THF (10.0 mL). Column chromatography (hexane/CH_2Cl_2 7:3 *v*/*v* + 4% triethylamine, R_f = 0.25) afforded **(*R*)-17** as a colourless oil (23.8 mg, 89%). $[\alpha]_D^{20}$ -26 (*c* 0.5, $CHCl_3$); lit.[5] $[\alpha]_D^{24}$ +69 (*c* 0.65, $CHCl_3$, *ent*).

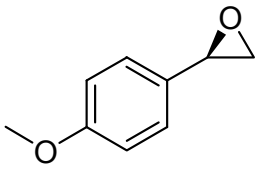
The NMR spectra of **(*R*)-17** were consistent with those previously reported:[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19-7.07 (m, 4H,), 4.02 (dd, J = 4.0, 2.8 Hz, 1H), 3.18 (dd, J = 5.7, 4.0 Hz, 1H), 2.71 (dd, J = 5.7, 2.8 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.7, 135.4, 129.3, 127.2, 125.7, 123.6, 50.0, 49.7, 18.3.

HRMS (EI): calcd. for $[M]^+$ $C_9H_{10}O$ requires 134.0732, found 134.0729.

4.4 (*R*)-2-(4-methoxyphenyl)oxirane [(*R*)-18]



Prepared according to general procedure A using **10** (20 µL, 0.17 mmol), **(*S*,*S*)-7f** (217 mg, 0.17 mmol), P_2-*t*Bu base (85 µL) and THF (8.5 mL). Column chromatography (hexane/CH_2Cl_2 8:2 + 5% triethylamine, R_f = 0.2) afforded **(*R*)-18** as a colourless oil (20.4 mg, 80%). $[\alpha]_D^{20}$ -26 (*c* 1, $CHCl_3$); lit.[6] $[\alpha]_D^{20}$ -29 (*c* 1, $CHCl_3$).

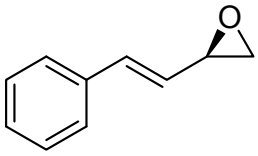
The NMR spectra of **(*R*)-18** were consistent with those previously reported:[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 3.90-3.82 (m, 4H), 3.14 (dd, J = 5.0, 4.5 Hz, 1H), 2.82 (dd, J = 5.0, 2.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 129.3, 126.7, 113.8, 55.1, 52.0, 50.8.

HRMS (EI): calcd. for $[M]^+$ $C_9H_{10}O_2$ requires 150.0681, found: 150.0686.

4.5 (*R*)-2-[(*E*)-styryl]oxirane [(*R*)-19]

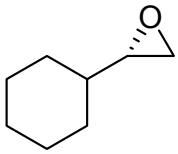


Prepared according to general procedure A using **11** (21 µL, 0.17 mmol), **(*S*,*S*)-7f** (217 mg, 0.17 mmol), P_2-*t*Bu base (85 µL) and THF (8.5 mL). Column chromatography (hexane/CH_2Cl_2 8:2 *v*/*v* + 5% triethylamine, R_f = 0.2) afforded **(*R*)-19** as a colourless oil (21.7 mg, 88%). $[\alpha]_D^{20}$ +9 (*c* 0.2, acetone); lit.[7] $[\alpha]_D^{20}$ +15.6 (*c* 3, acetone).

The NMR spectra of **(*R*)-19** were consistent with those previously reported:[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.29 (m, 5H), 6.83 (d, J = 16.3 Hz, 1H), 5.88 (dd, J = 16.3, 8.0 Hz, 1H), 3.59-3.51 (m, 1H), 3.08 (app. t, 1H), 2.80 (dd, J = 5.1, 2.6 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 134.1, 128.2, 127.6, 126.5, 125.9, 52.2, 48.8.
HRMS (EI): calcd. for $[M]^+$ $C_{10}H_{10}O$ requires 146.0732, found 146.0726.

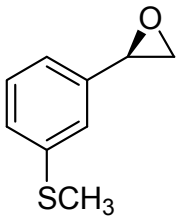
4.6 (*S*)-2-cyclohexyloxirane [(*S*)-20]



Prepared according to general procedure A using **12** (24 µL, 0.20 mmol), **(*R*,*R*)-7f** (256 mg, 0.20 mmol), P_2-*t*Bu base (100 µL) and THF (10.0 mL). Column chromatography (hexane/EtOAc 95:5 *v*/*v*, R_f = 0.4) afforded **(*S*)-20** as a colourless oil (18.9 mg, 75%). $[\alpha]_D^{20}$ +1.5 (*c* 1.0, $CHCl_3$); lit.[8] $[\alpha]_D^{20}$ +2.2 (*c* 10.5, $CHCl_3$).
The NMR spectra of **(*S*)-20** were consistent with those previously reported:[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.77-2.72 (m, 2H), 2.55 (dd, J = 4.4, 3.8 Hz, 1H), 1.89 (m, 1H), 1.69-1.78 (m, 4H), 1.10-1.31 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.3, 45.6, 39.9, 29.3, 28.3, 25.8, 25.2, 25.1.
HRMS (EI): calcd. for $[M]^+$ $C_8H_{14}O$ requires 126.1045, found 126.1041.

4.7 (*R*)-2-(3-methylthiophenyl)oxirane [(*R*)-21]

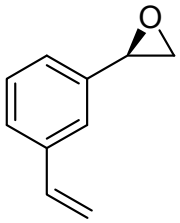


Prepared according to general procedure A using **13**[9] (30 mg, 0.20 mmol), **(*S*,*S*)-7f** (256 mg, 0.20 mmol), P_2-*t*Bu base (100 µL) and THF (10.0 mL). Column chromatography (hexane/EtOAc 95:5 *v*/*v*, R_f = 0.2) afforded **(*R*)-21** as a colourless oil (29.2 mg, 88%). The configuration was assigned to be (*R*) by analogy with the other entries.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.25 (m, 1H), 7.23-7.16 (m, 2H), 7.08 (d, J = 7.5 Hz, 1H), 3.88-3.84 (m, 1H), 3.16 (app t, 1H), 2.80 (dd, J = 5.5, 2.6 Hz, 1H), 2.51 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 134.1, 129.4, 127.9, 125.1, 123.3, 51.3, 50.8, 15.9.

HRMS (EI): calcd. for $[M]^+$ $C_9H_{10}OS$ requires 166.0452, found 166.0452.

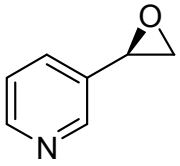
4.8 (*R*)-2-(3-vinylphenyl)oxirane [(*R*)-22]



Prepared according to general procedure A using **14** (28.5 µL, 0.22 mmol), **(*S*,*S*)-7f** (281 mg, 0.22 mmol), P_2-*t*Bu base (110 µL) and THF (11.0 mL). Column chromatography (hexane/CH_2Cl_2 8:2 *v*/*v*, R_f = 0.2) afforded **(*R*)-22** as a colourless oil (30.2 mg, 94%). $[\alpha]_D^{20}$ +11 (*c* 0.3, $CHCl_3$). The configuration was assigned to be (*R*) by analogy with the other entries. The NMR spectra of **(*R*)-22** were consistent with those previously reported:[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.30 (m, 3H), 7.20 (d, *J* = 7.7 Hz, 1H), 6.73 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.79 (d, *J* = 17.5 Hz, 1H), 5.30 (d, *J* = 11.1 Hz, 1H), 3.89 (app t, 1H), 3.18 (app t, 1H), 2.83 (dd, *J* = 5.6, 2.8 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.47, 137.42, 136.0, 128.3, 125.6, 124.5, 122.7, 113.9, 51.8, 50.7.
HRMS (ESI): calcd. for $[M+H]^+$ $C_{10}H_{11}O$ requires 147.0810, found 147.0806.

4.9 (*R*)-2-(3-pyridyl)oxirane [(*R*)-23]



Prepared according to general procedure A using **15** (19.5 µL, 0.21 mmol), **(*S*,*S*)-7f** (269 mg, 0.21 mmol), P_2-*t*Bu base (105 µL) and THF (14.0 mL). Column chromatography (hexane/CH_2Cl_2 8:2 *v*/*v*, R_f = 0.2) afforded **(*R*)-23** as a colourless oil (22.6 mg, 89%). $[\alpha]_D^{20}$ -13 (*c* 0.2, $CHCl_3$); lit.[11] $[\alpha]_D^{20}$ +18.3 (*c* 0.9, $CHCl_3$, *ent*).
The NMR spectra of **(*R*)-23** were consistent with those previously reported:[11]

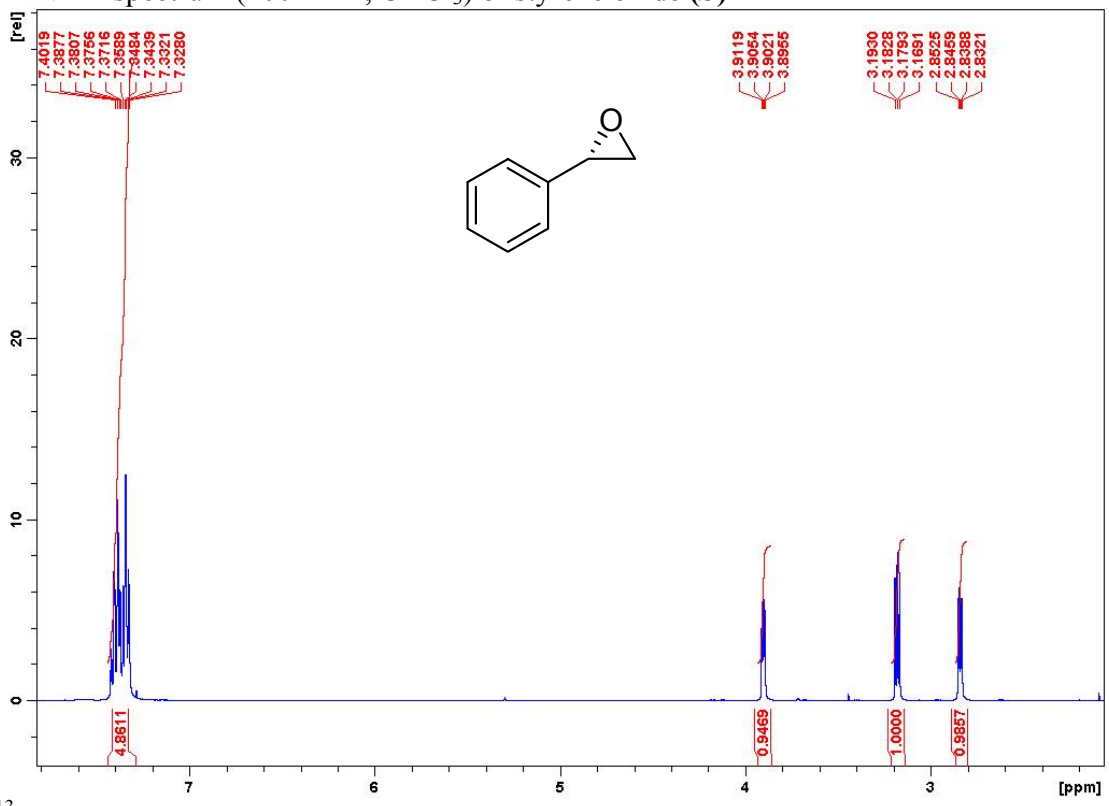
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 8.58 (dd, J = 4.9, 1.6 Hz, 1H), 7.57 (dd, J = 7.8, 1.6 Hz, 1H), 7.30 (dd, J = 7.8, 4.9 Hz, 1H), 3.92 (dd, J = 3.7, 2.7 Hz, 1H), 3.22 (dd, J = 5.3, 3.7 Hz, 1H), 2.85 (dd, J = 5.3, 2.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6, 147.8, 133.2, 132.6, 123.4, 51.0, 50.3.

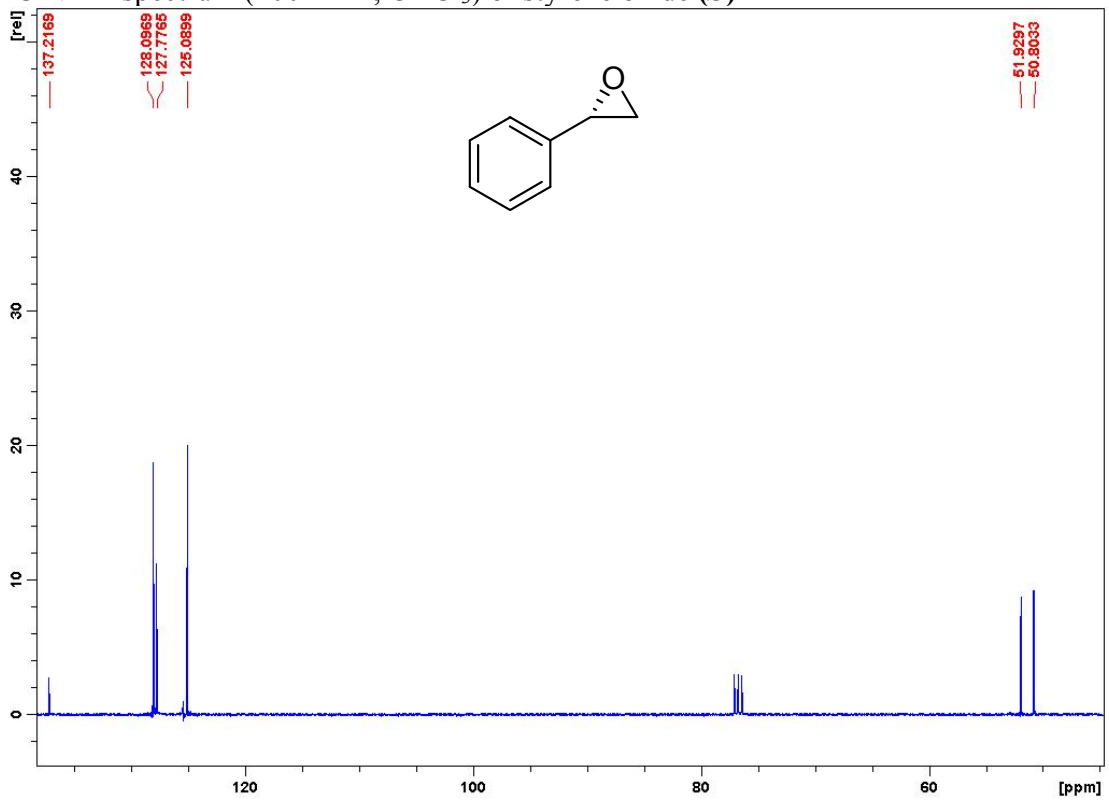
HRMS (ESI): calcd. for $[M+H]^+$ C_7H_8NO requires 122.0606, found: 122.0600.

5.0 NMR spectra

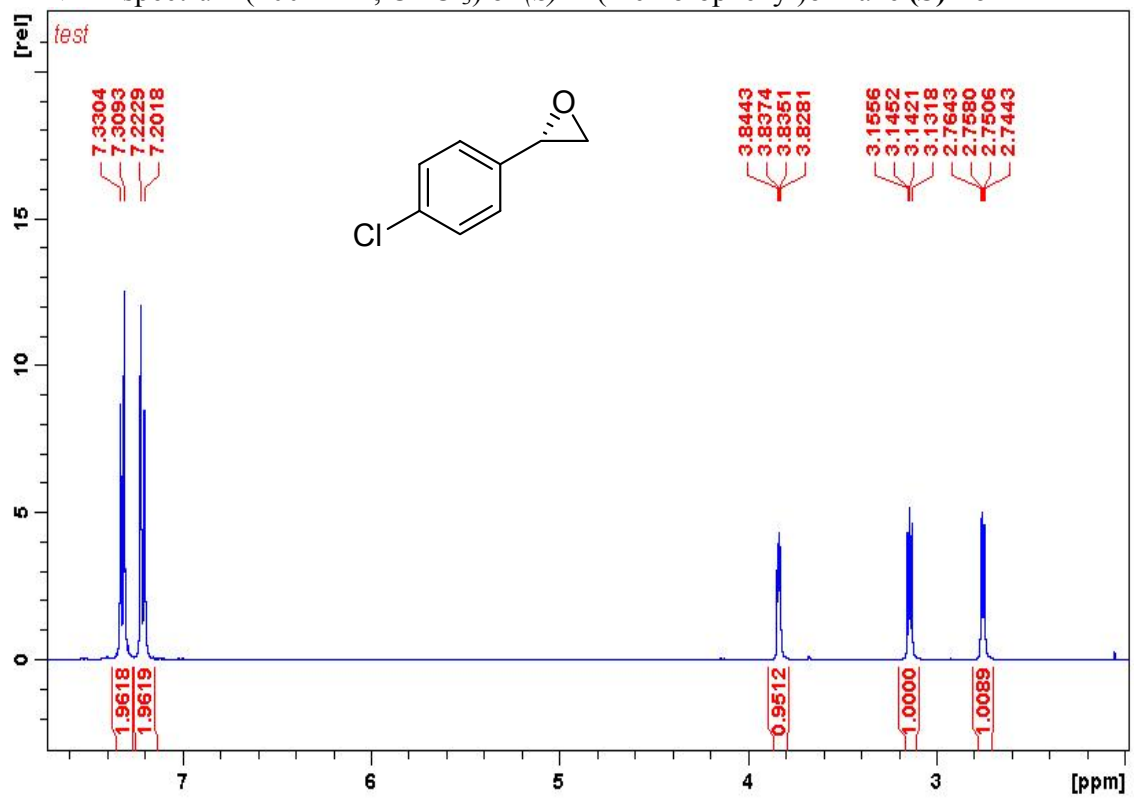
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of styrene oxide **(*S*)-2**



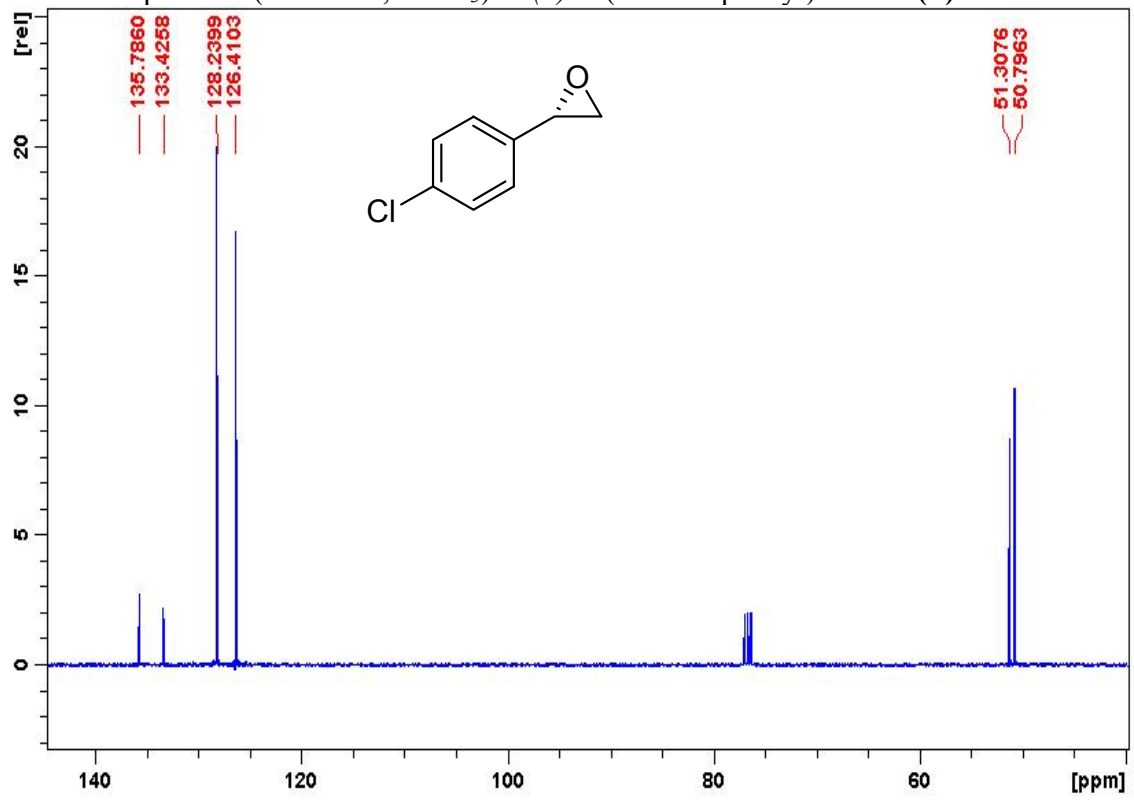
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of styrene oxide **(*S*)-2**



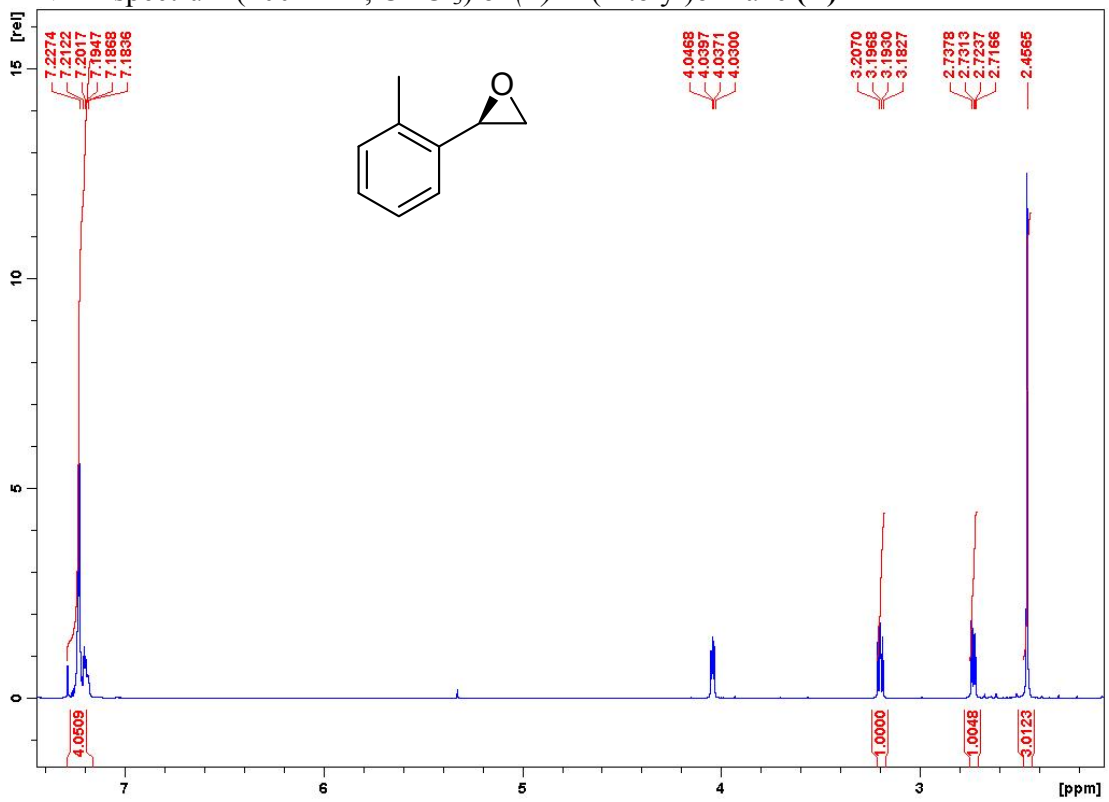
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *(S)-2*-(4-chlorophenyl)oxirane **(*S*)-16**



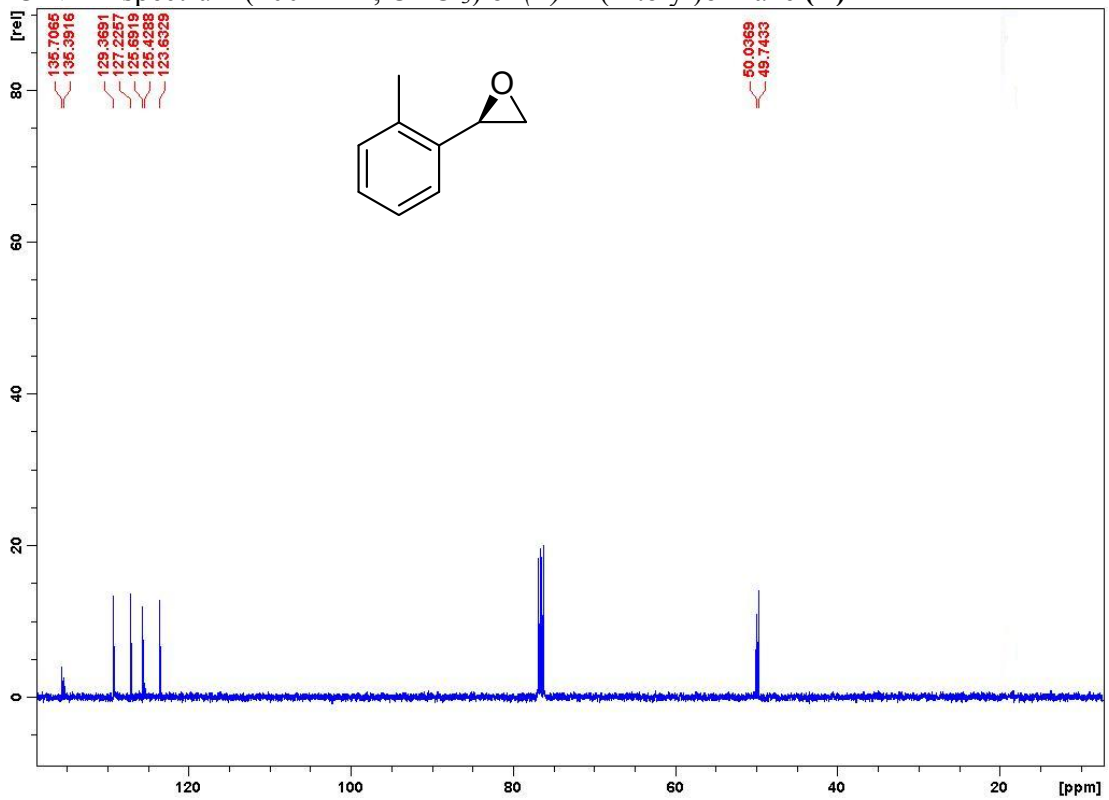
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *(S)-2*-(4-chlorophenyl)oxirane **(*S*)-16**



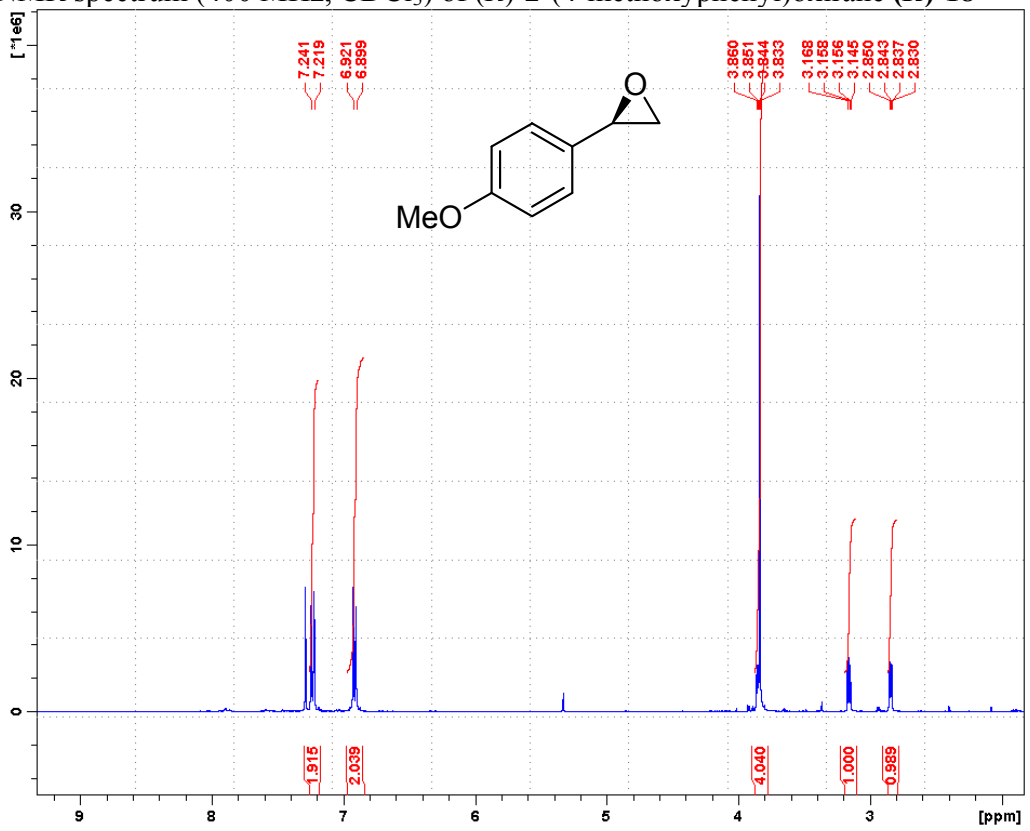
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *(R)*-2-(2-tolyl)oxirane **(*R*)-17**



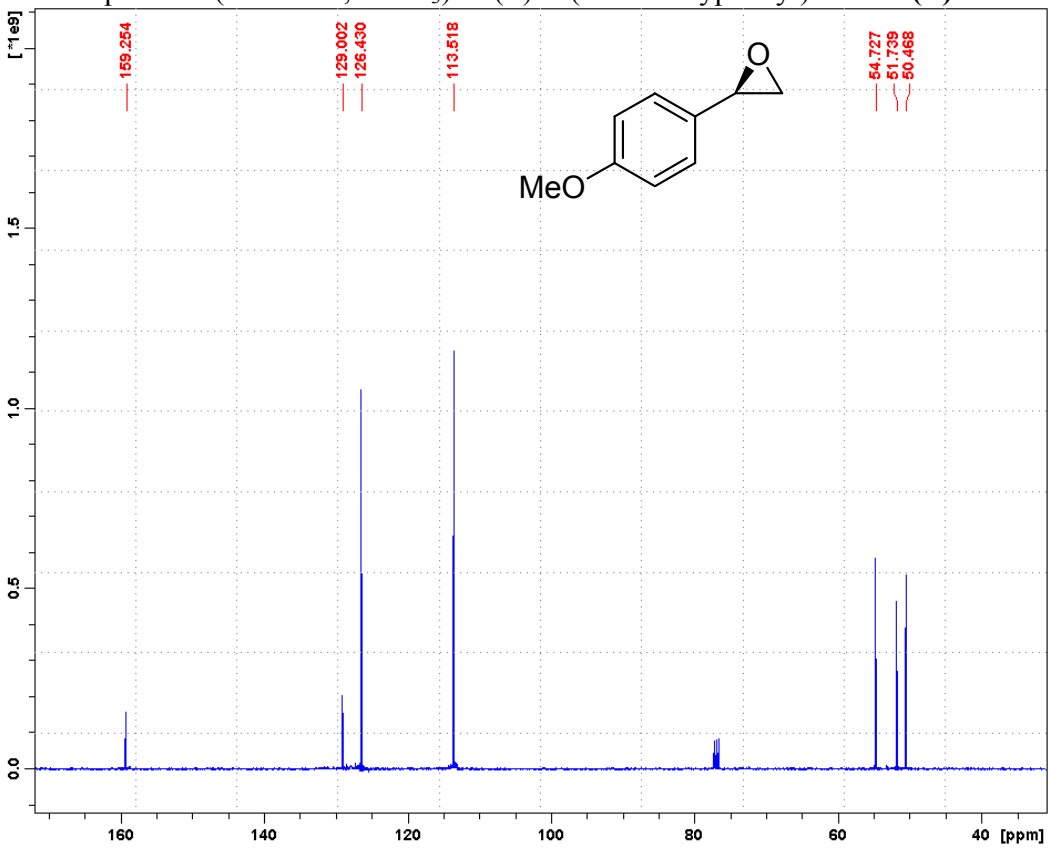
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *(R)*-2-(2-tolyl)oxirane **(*R*)-17**



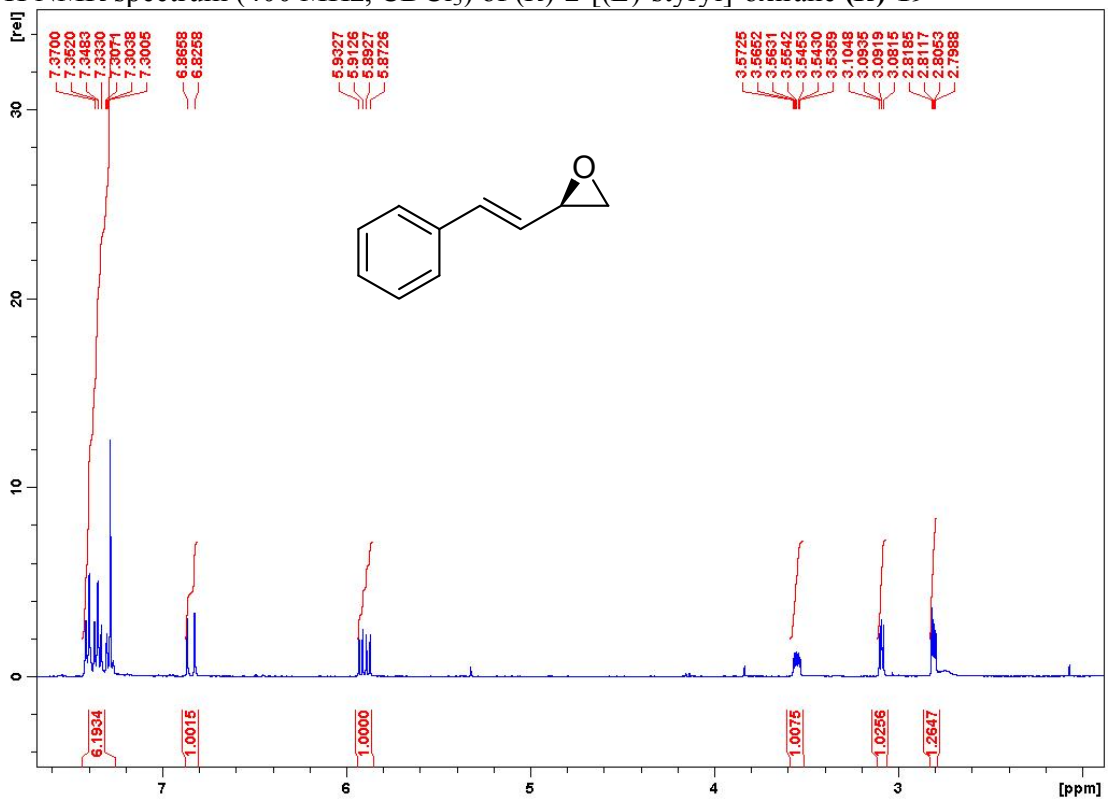
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R*)-2-(4-methoxyphenyl)oxirane **(*R*)-18**



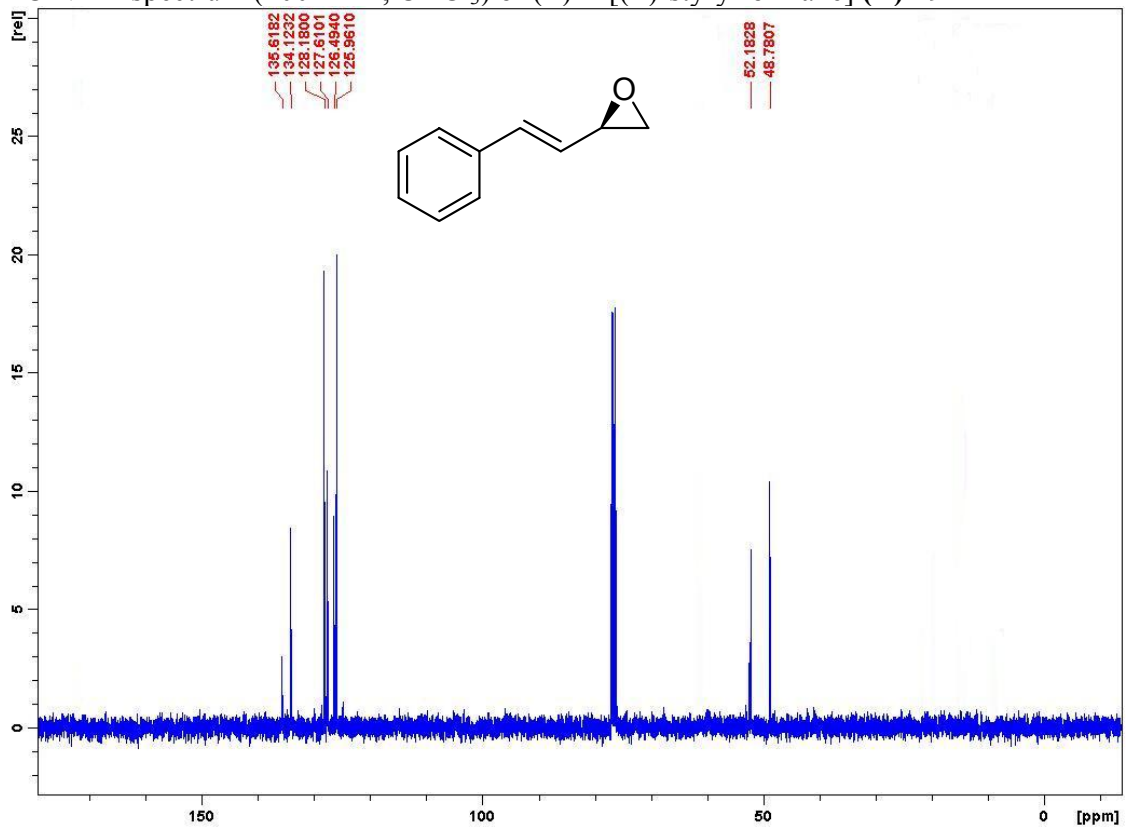
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R*)-2-(4-methoxyphenyl)oxirane **(*R*)-18**



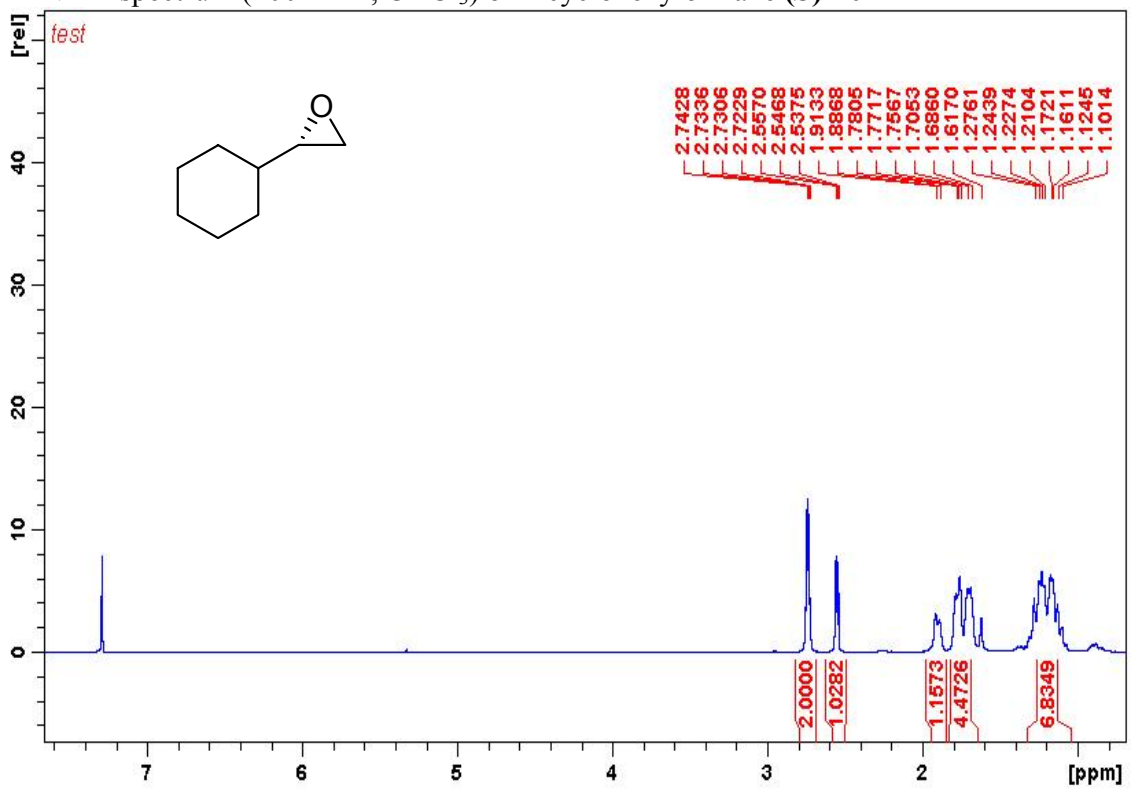
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (*R*)-2-[(*E*)-styryl]-oxirane **(*R*)-19**



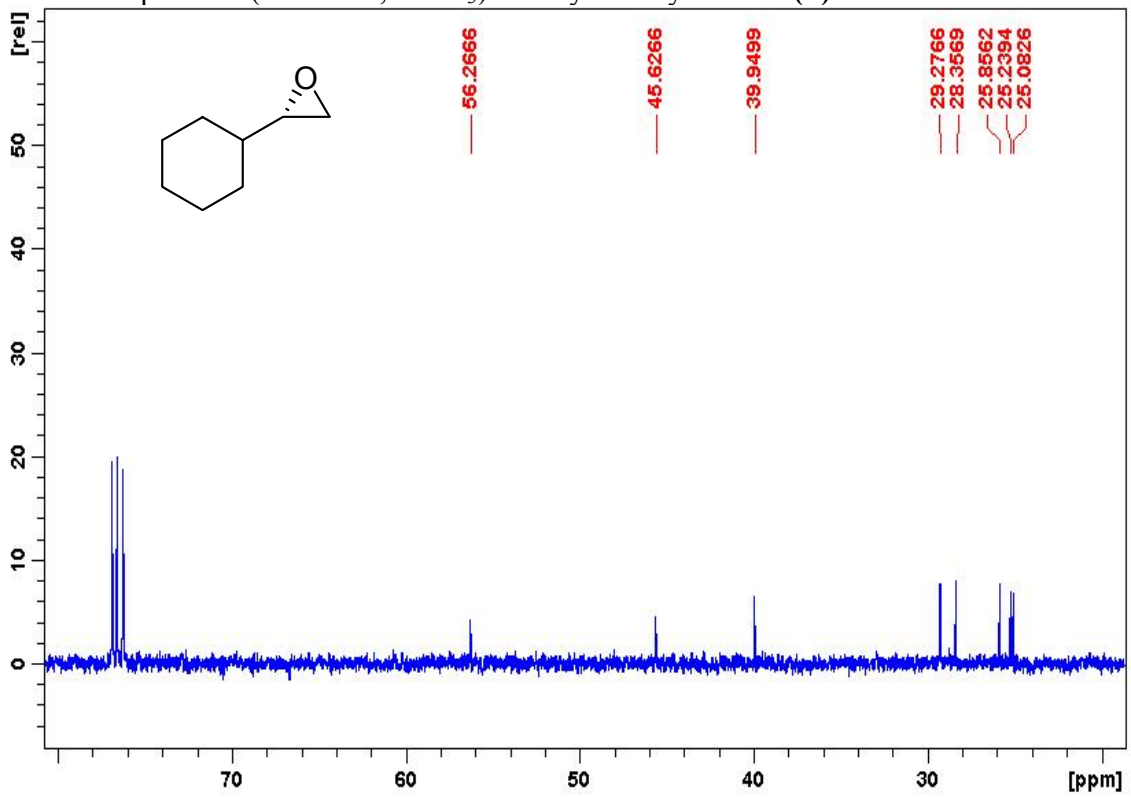
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (*R*)-2-[(*E*)-styryl-oxirane] **(*R*)-19**



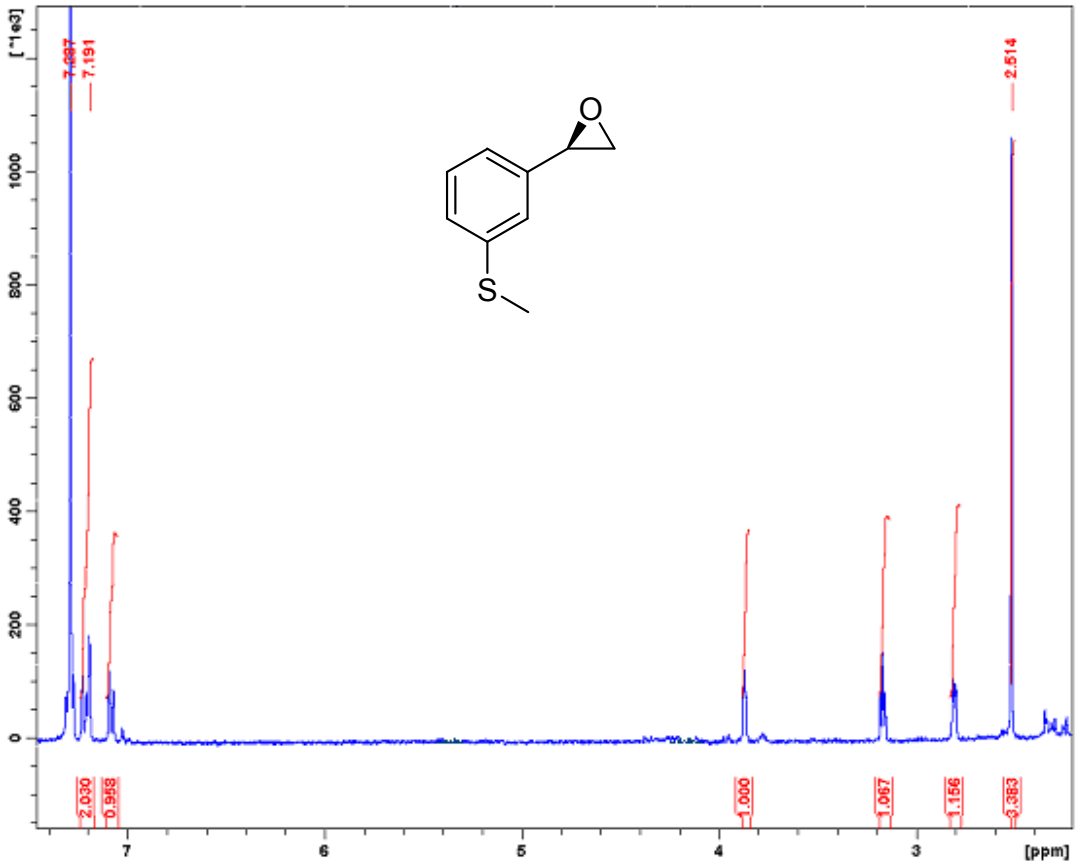
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-cyclohexyloxirane **(*S*)-20**



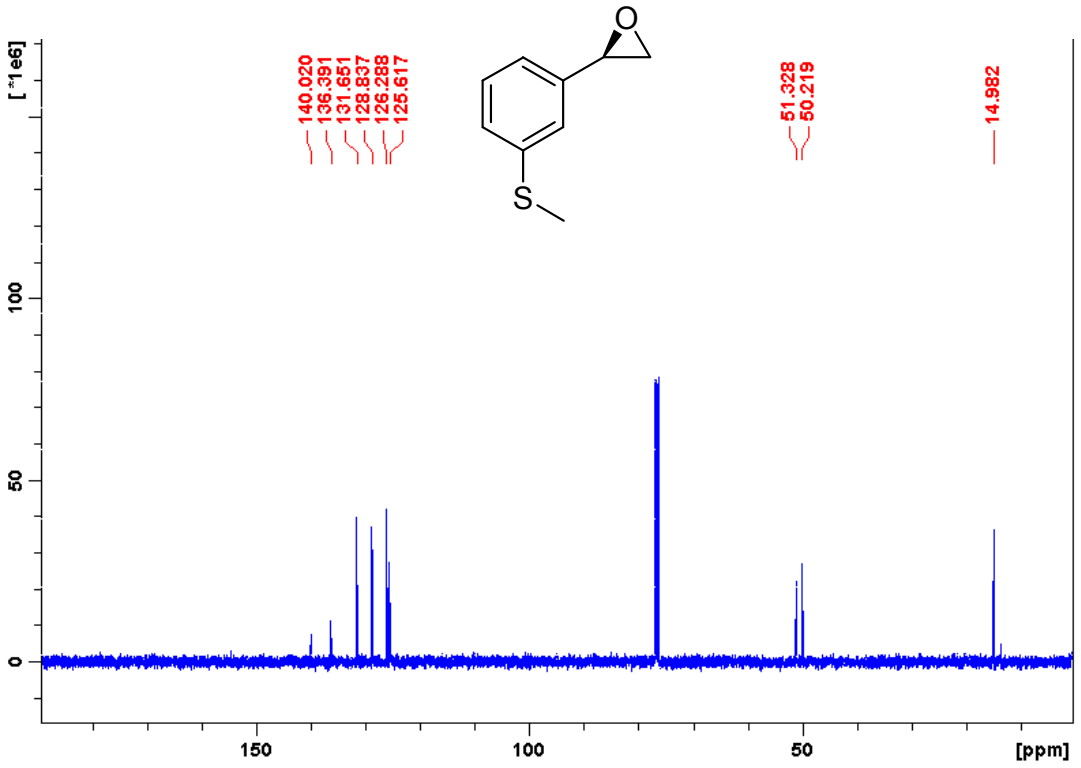
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 2-cyclohexyloxirane **(*S*)-20**



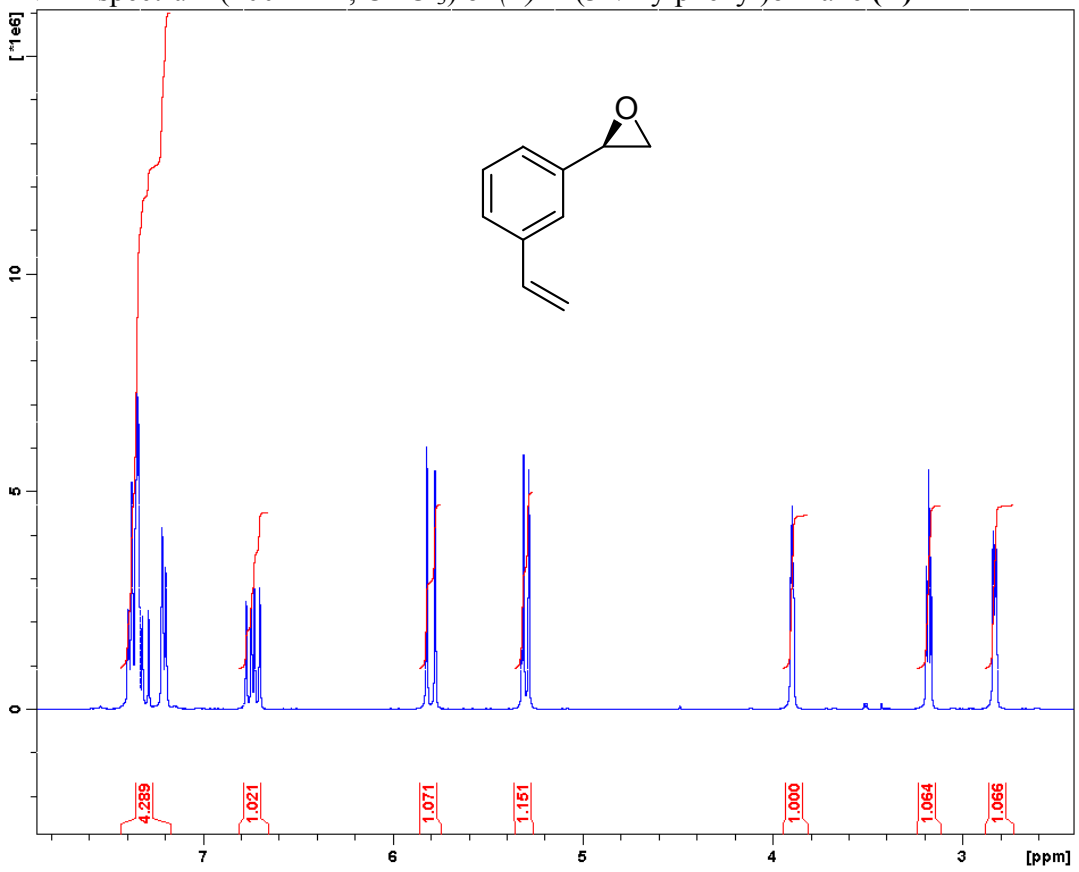
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *(R)*-3-(3-methylthiophenyl)oxirane ***(R)*-21**



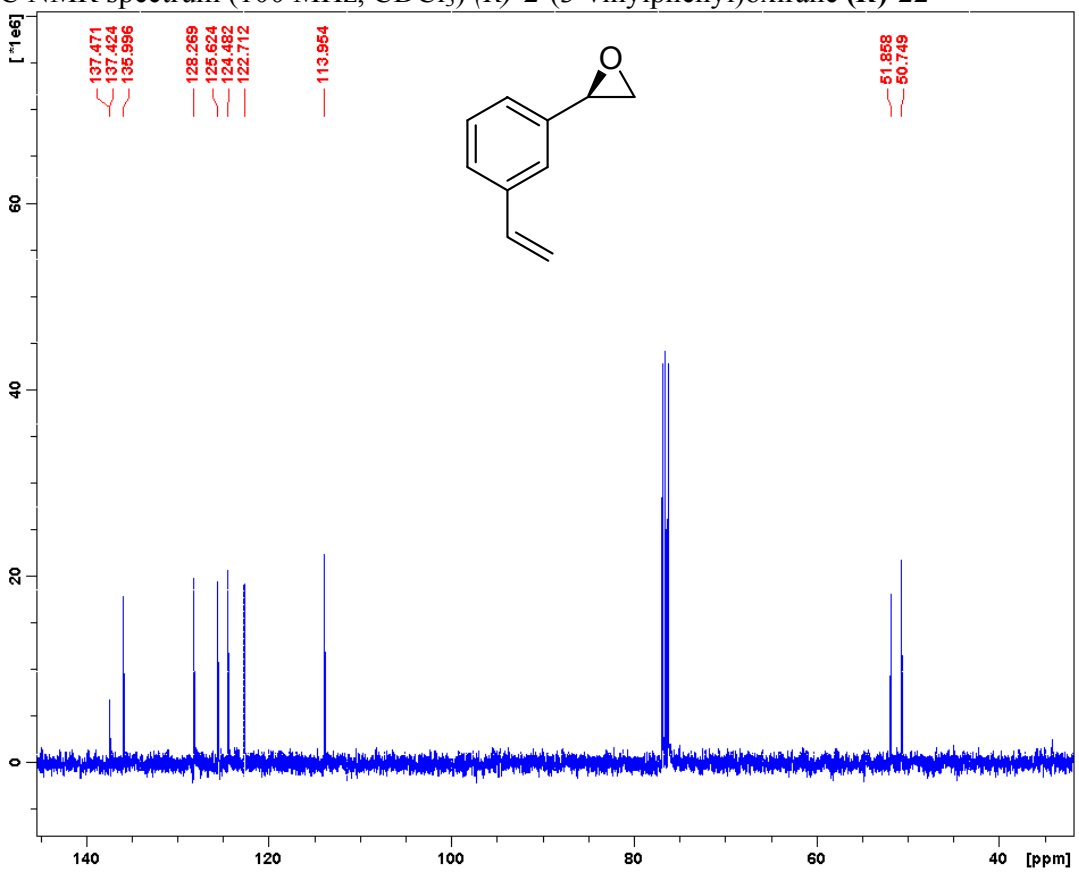
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *(R)*-3-(3-methylthiophenyl)oxirane **(*R*)-21**



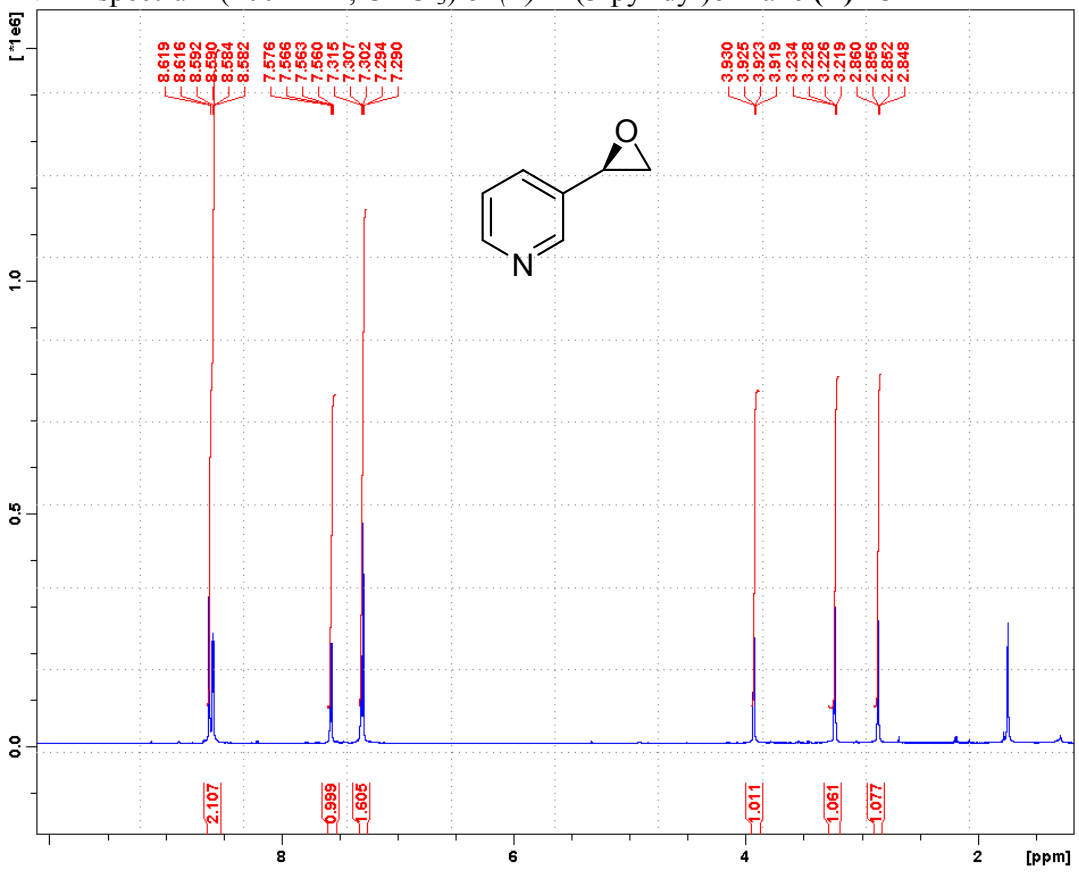
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *(R)*-2-(3-vinylphenyl)oxirane **(*R*)-22**



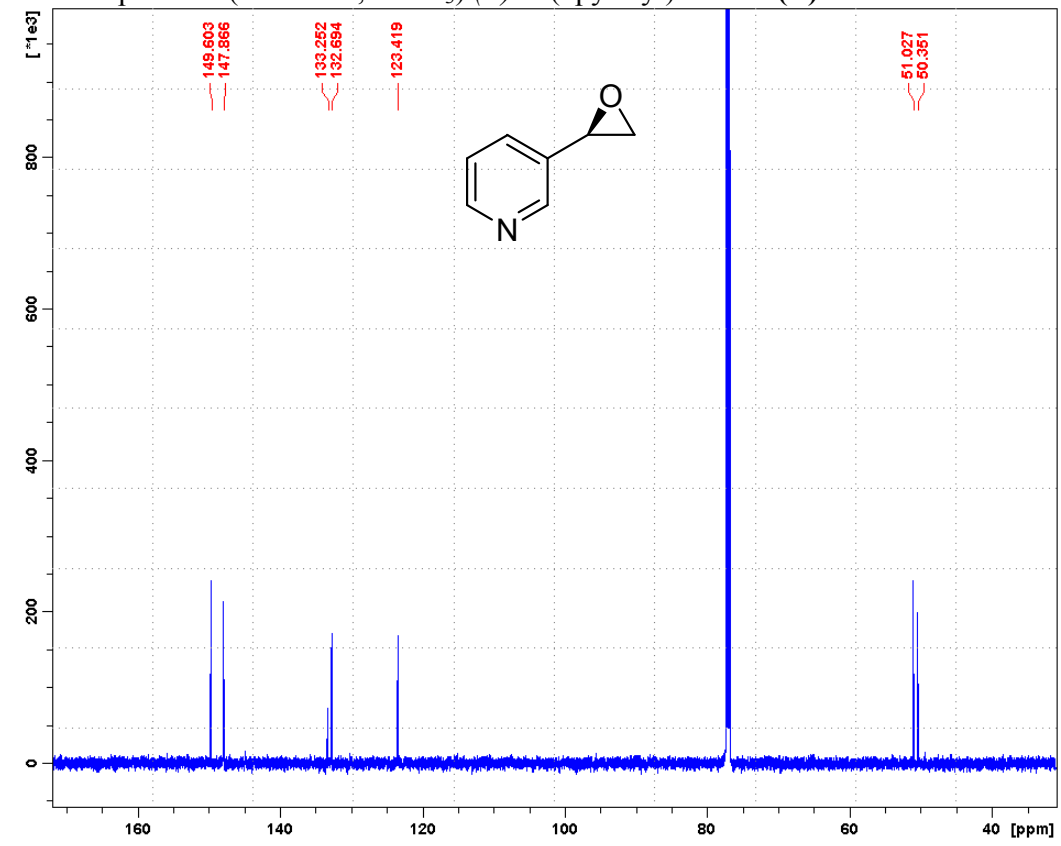
^{13}C NMR spectrum (100 MHz, $CDCl_3$) *(R)*-2-(3-vinylphenyl)oxirane **(*R*)-22**



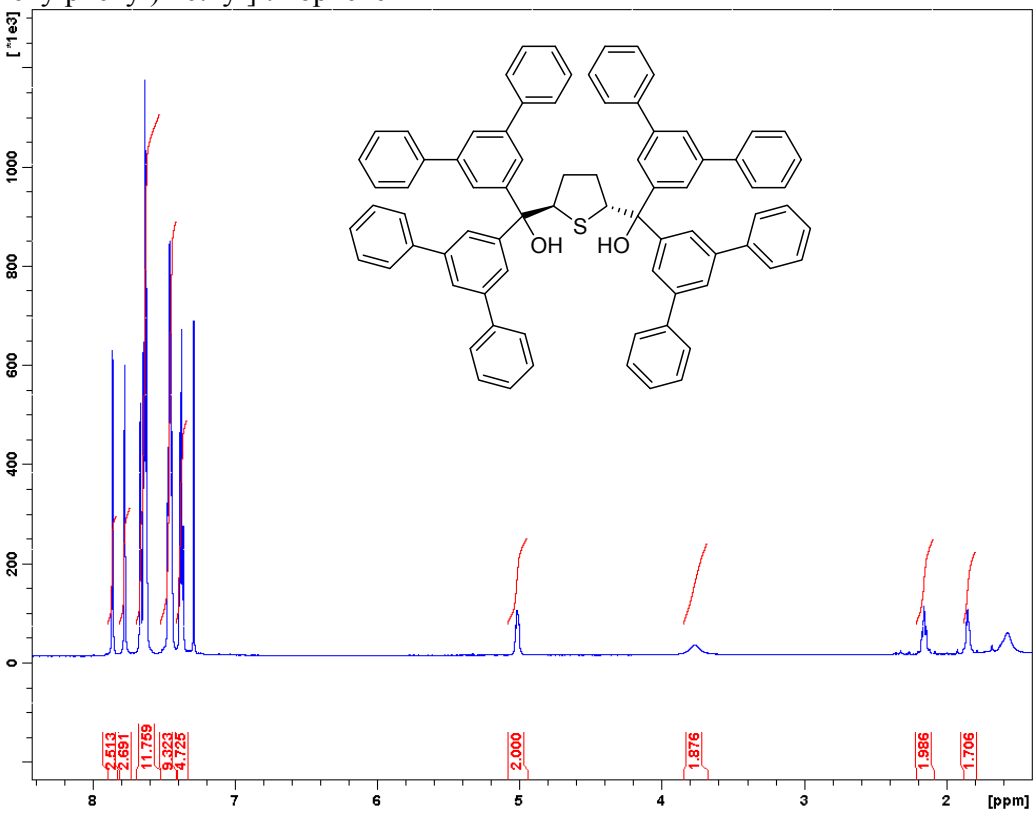
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *(R)*-2-(3-pyridyl)oxirane **(*R*)-23**



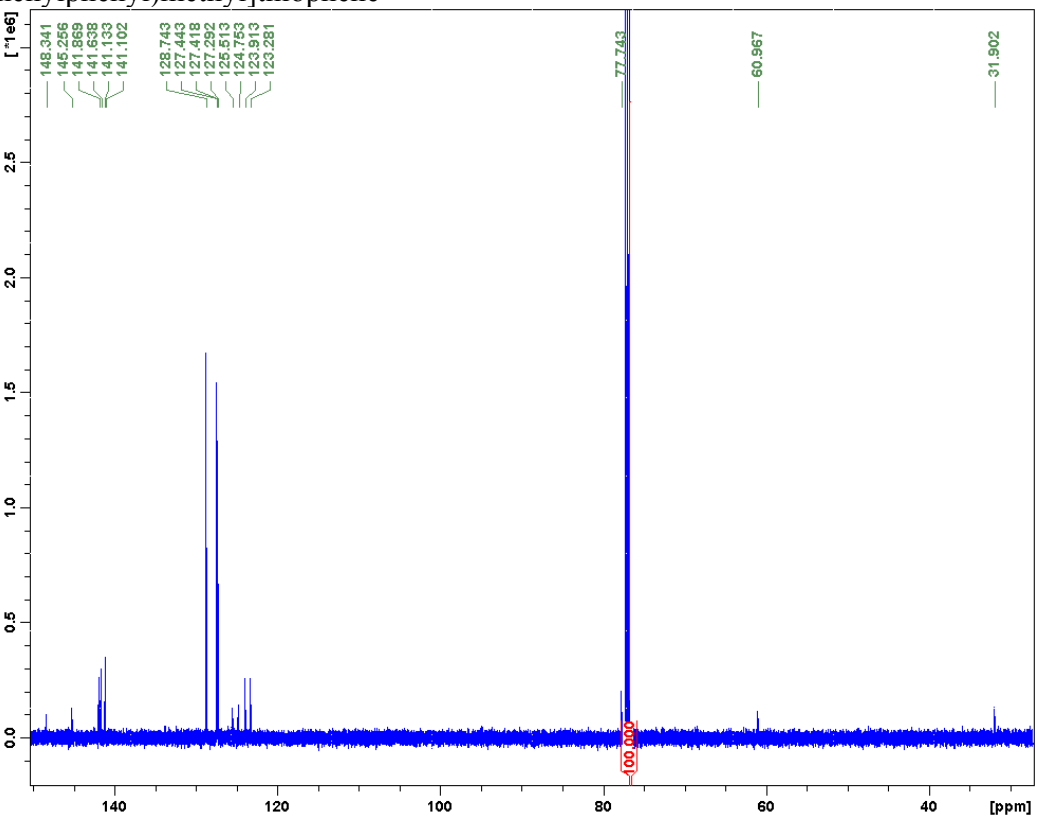
^{13}C NMR spectrum (100 MHz, $CDCl_3$) *(R)*-2-(3pyridyl)oxirane **(*R*)-23**



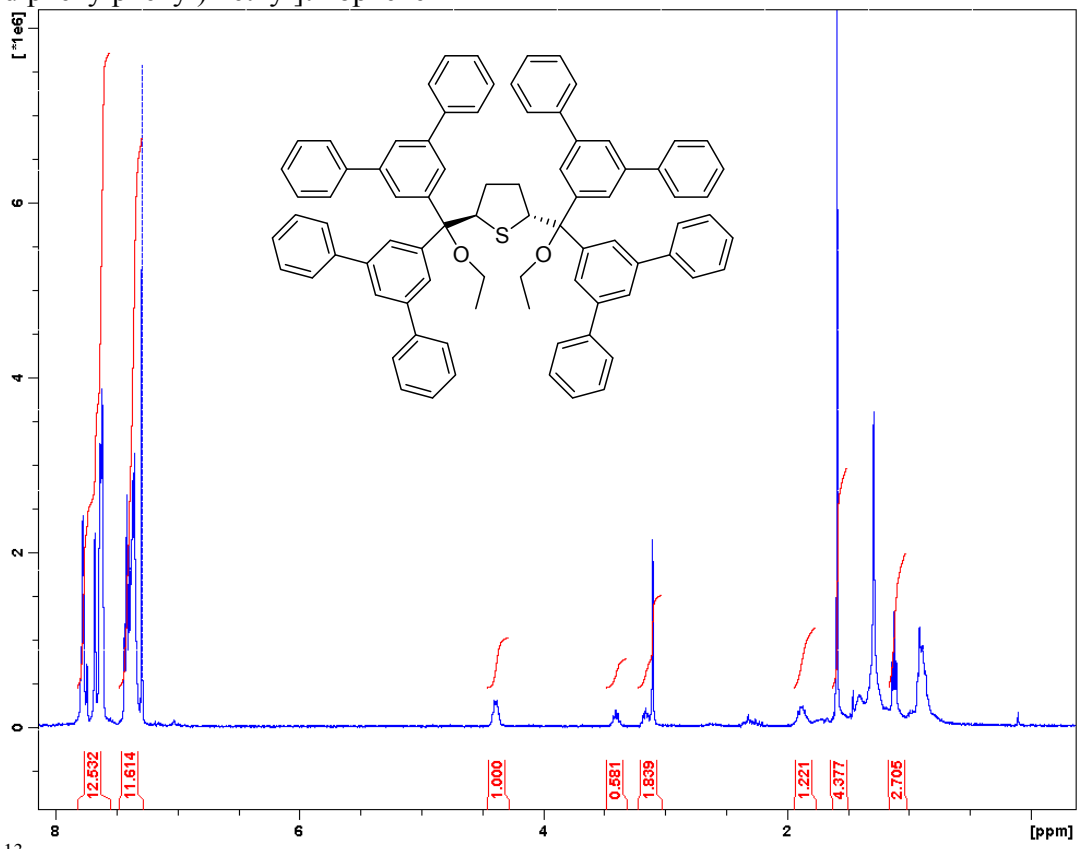
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (2*R*,5*R*)-Tetrahydro-2,5-[hydroxy-*bis*-(3,5-diphenylphenyl)methyl] thiophene



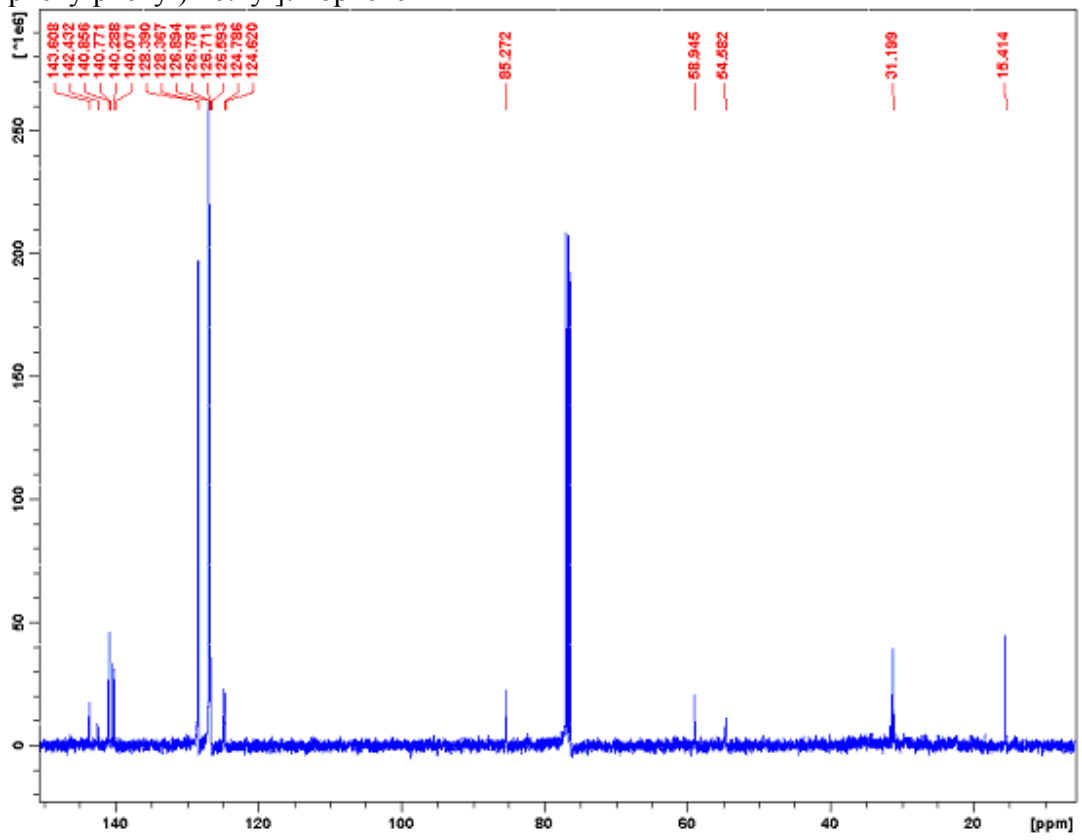
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (2*R*,5*R*)-Tetrahydro-2,5-[hydroxy-*bis*-(3,5-diphenylphenyl)methyl]thiophene



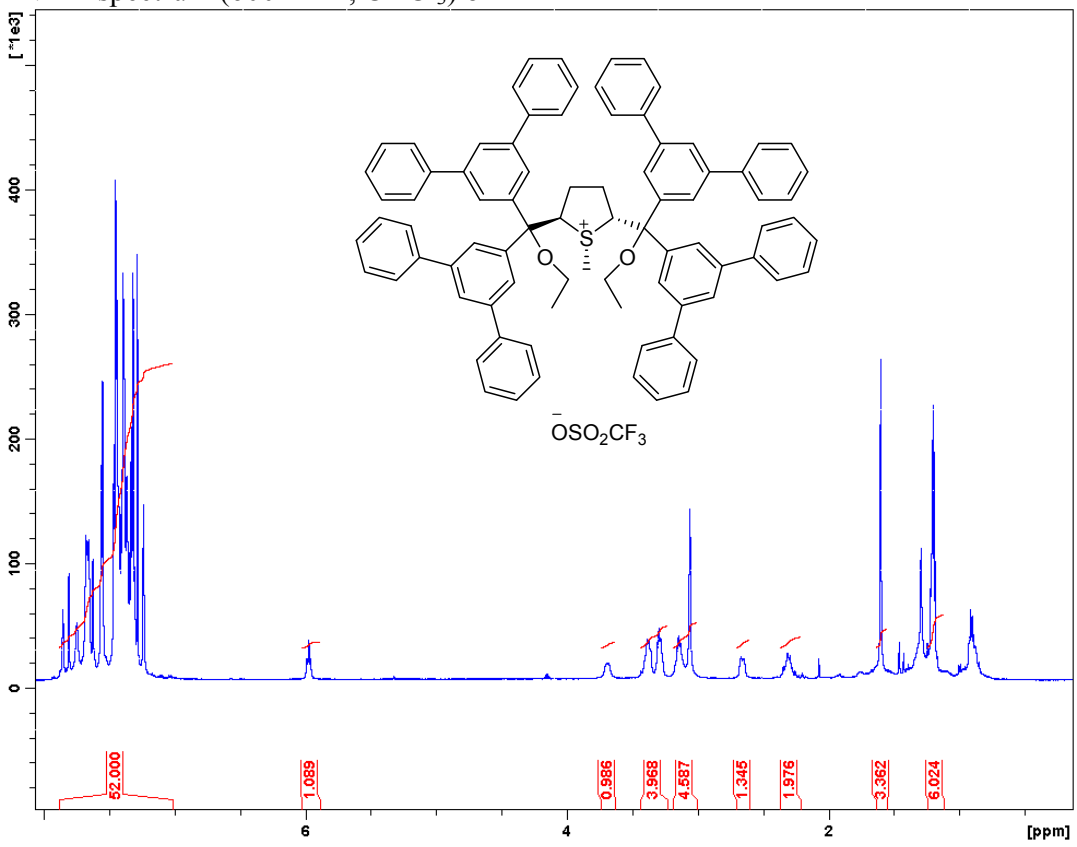
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (2*R*,5*R*)-Tetrahydro-2,5-[ethoxy-*bis*-(3,5-diphenylphenyl)methyl]thiophene



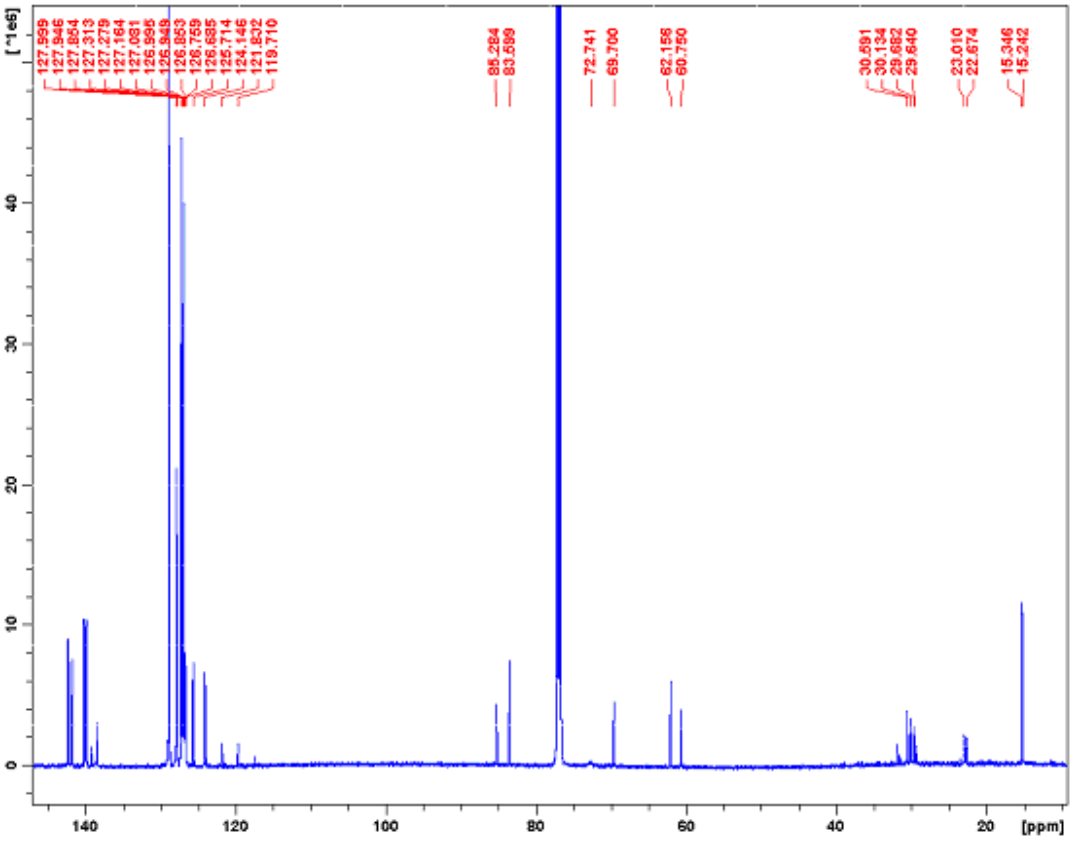
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (2*R*,5*R*)-Tetrahydro-2,5-[ethoxy-*bis*-(3,5-diphenylphenyl)methyl]thiophene



^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **7f**



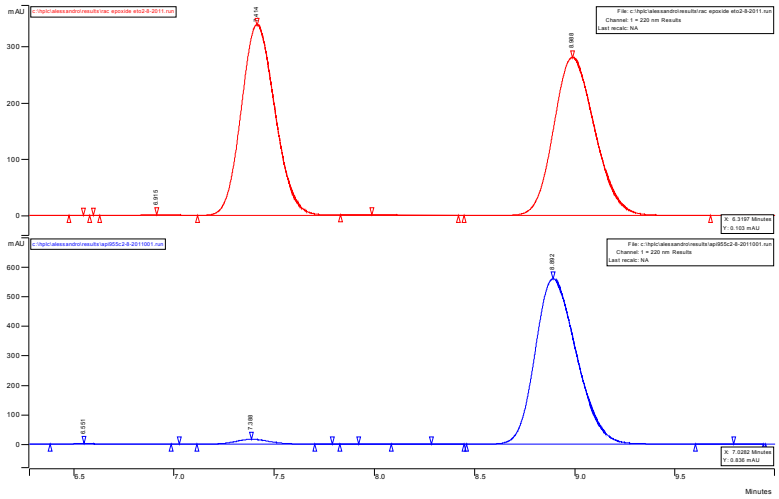
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of **7f**



6.0 HPLC chromatograms

6.1 (*S*)-2-phenyloxirane [(*S*)-2]

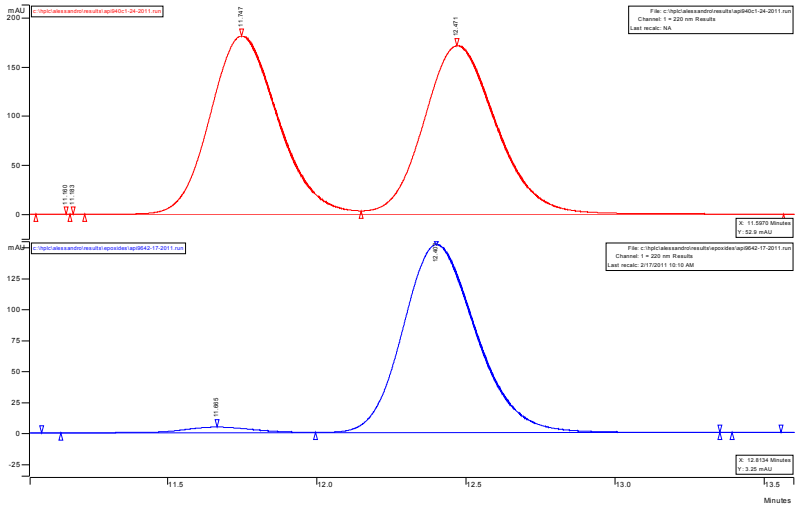
95% *ee* as determined by CSP-HPLC analysis: Chiralpak AS (4.6 mm x 25 cm), hexane/IPA: 99/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 7.4 min (minor enantiomer) and 8.9 (major enantiomer).



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		7.387	2.2719	0.000	0.00	1770433	BB	10.5		0
2		8.890	97.7281	0.000	0.00	76158584	BB	13.1		0
	Totals		**100.0000**	**0.000**		**77929016**				

6.2 (*S*)-*2*-(4-chlorophenyl)oxirane [(*S*)-16]

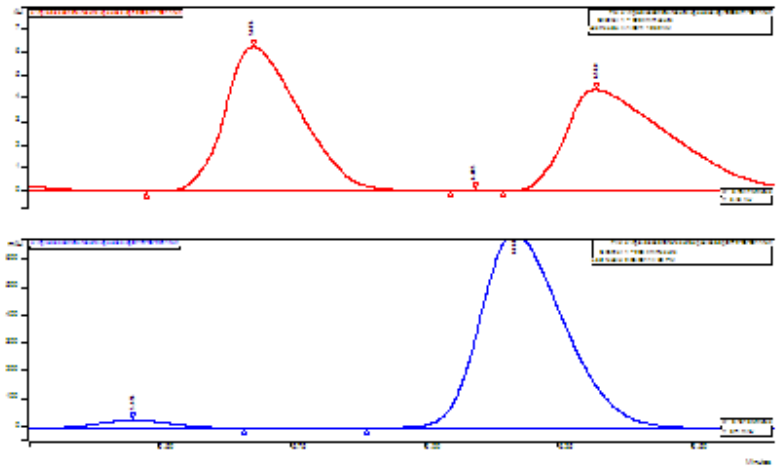
95% *ee* as determined by CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 0.5 mL min^{-1}, RT, UV detection at 220 nm, retention times: 11.7 min (minor enantiomer) and 12.4 (major enantiomer).



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		11.665	2.5161	0.000	0.00	668924	BB	14.7		0
2		12.401	97.4839	0.000	0.00	25916968	BB	15.7		0
	Totals		**100.0000**	**0.000**		**26585892**				

6.3 (*R*)-2-(2-tolyl)oxirane [(*R*)-17]

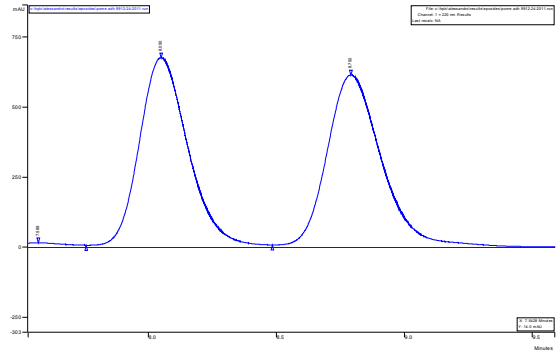
93% *ee* as determined by CSP-HPLC analysis: Chiralpak AS (4.6 mm x 25 cm), hexane/IPA: 99/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 5.4 min (minor enantiomer) and 6.2 (major enantiomer).

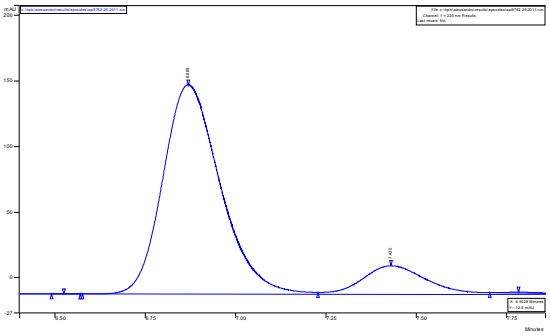


Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		5.453	3.2510	0.000	0.00	2469689	BB	8.1		0
2		6.168	96.7490	0.000	0.00	73498064	BB	10.0		0
	Totals		**100.0000**	**0.000**		**75967752**				

6.4 (*R*)-2-(4-mehoxyphenyl)oxirane [(*R*)-18]

72% *ee* as determined by CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 6.9 min (major enantiomer) and 7.4 (minor enantiomer).

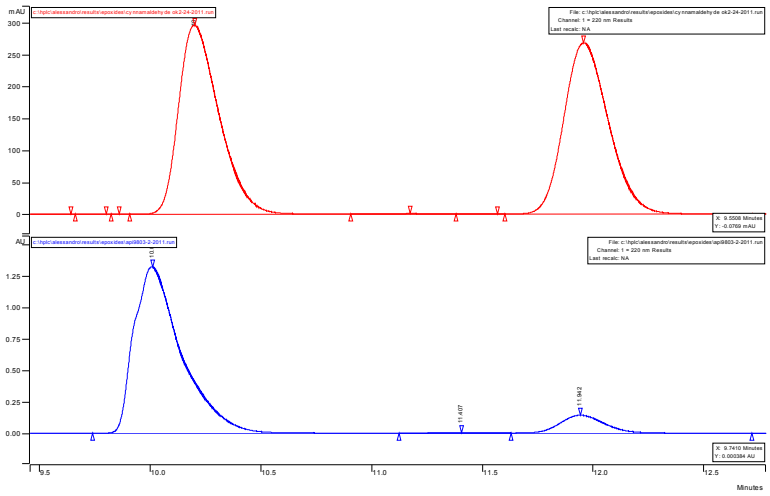




Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		6.868	85.9156	0.000	0.00	14844234	BB	9.5		0
2		7.430	14.0844	0.000	0.00	2433461	BB	10.5		0
	Totals		**100.0000**	**0.000**		**17277696**				

6.5 (*R*)-2-[(*E*)-styryl]oxirane [(*R*)-19]

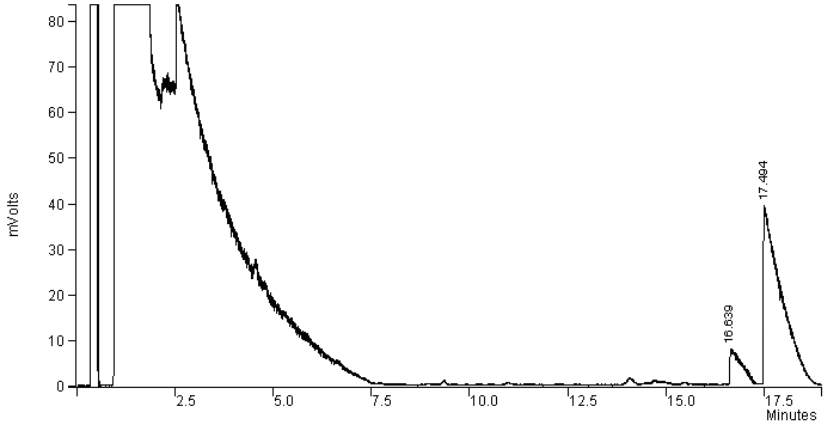
82% *ee* as determined by CSP-HPLC analysis: Chiralcel OD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 10.0 min (major enantiomer) and 11.9 (minor enantiomer).



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		10.005	91.0319	0.000	0.00	196232160	BB	13.4		0
2		11.941	8.9681	0.000	0.00	19332052	BB	12.7		0
	Totals		**100.0000**	**0.000**		**215564208**				

6.6 (*S*)-2-cyclohexyloxirane [(*S*)-20]

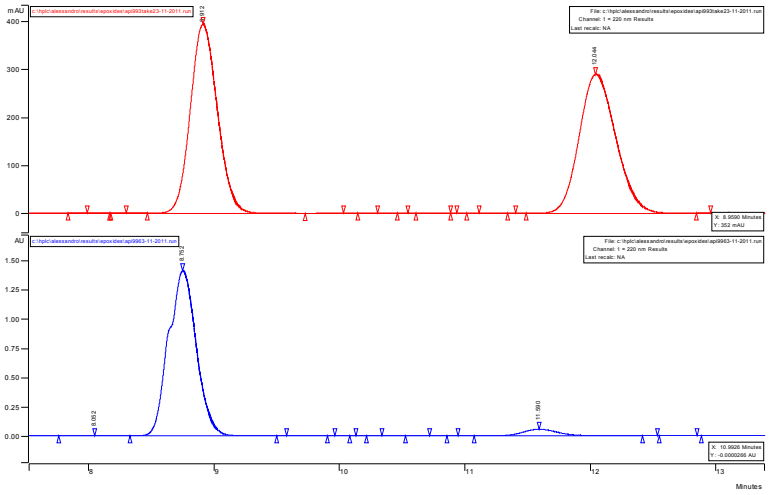
81% *ee* as determined by chiral GC analysis: Supelco cyclodextrin-β capillary column (betadex 120), 30 m × 0.25 mm i.d., 0.25 μm film. Isothermal 60 °C. Retention times: 16.6 min (minor enantiomer) and 17.5 (major enantiomer).



Peak No	Ret. Time (min)	Peak Name	Area (counts)	Result (%)
1	11.451		234	0.02
2	16.639		132538	9.90
3	17.494		1205462	90.08
		Totals	**1338234**	**100.00**

6.7 (*R*)-2-(3-methylthiophenyl)oxirane [(*R*)-21]

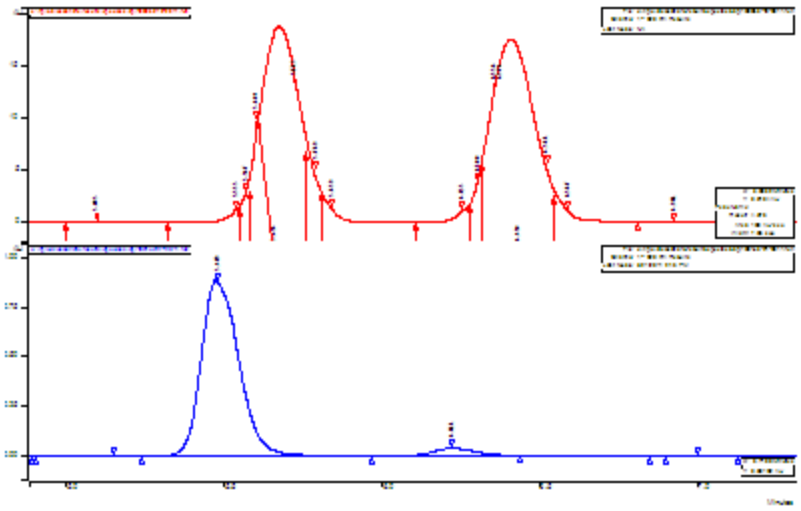
90% *ee* as determined by CSP-HPLC analysis: Chiralpak AS (4.6 mm x 25 cm), hexane/IPA: 99/1, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 8.8 min (major enantiomer) and 11.5 (minor enantiomer).



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		8.750	95.1187	0.000	0.00	217813504	BB	15.2		0
2		11.590	4.8813	0.000	0.00	11177660	BB	18.0		0
	Totals		**100.0000**	**0.000**		**228991168**				

6.8 (*R*)-2-(3-vinylphenyl)oxirane [(*R*)-22]

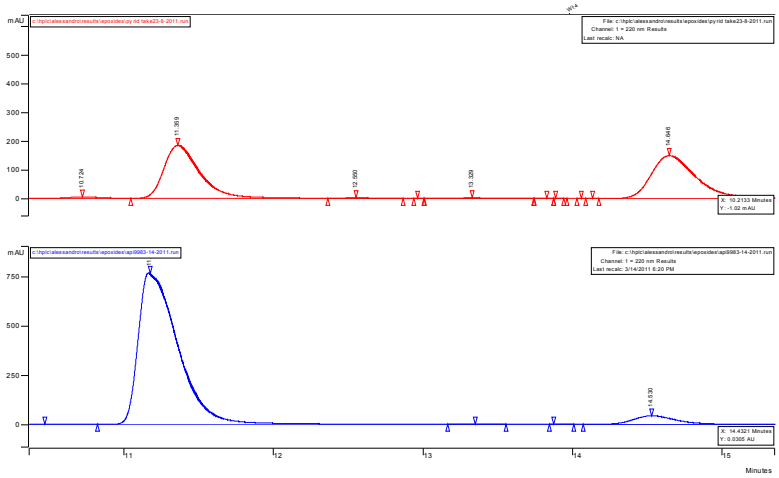
92% *ee* as determined by CSP-HPLC analysis: Chiralpak AD-H (4.6 mm x 25 cm), hexane/IPA: 99/1, 0.5 mL min^{-1}, RT, UV detection at 220 nm, retention times: 5.5 min (major enantiomer) and 6.2 (minor enantiomer).



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		5.470	95.8561	0.000	0.00	72465504	BB	7.7		0
2		6.220	4.1439	0.000	0.00	3132696	BB	8.1		0
	Totals		**100.0000**	**0.000**		**75598200**				

6.9 (*R*)-2-(3-pyridyl)oxirane [(*R*)-23]

90% *ee* as determined by CSP-HPLC analysis: Chiralcel OD-H (4.6 mm x 25 cm), hexane/IPA: 90/10, 1.0 mL min^{-1}, RT, UV detection at 220 nm, retention times: 11.1 min (major enantiomer) and 14.5 (minor enantiomer).



Peak No	Peak Name	Ret. Time (min)	Result ()	Time Offset (min)	Rel Ret Time	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		11.161	94.9790	0.000	0.00	141127664	BB	16.7		0
2		14.529	5.0210	0.000	0.00	7460655	BB	17.2		0
	Totals		**100.0000**	**0.000**		**148588320**				

References

1 K. Matsumoto, H. Keiichiro, N. Umezawa and T. Higuchi, *Synthesis* 2004, **13**, 2181.

2 E. Hauptman, R. Shapiro and W. Marshall, *Organometallics* 1998, **17**, 4976.

3 A. Archelas and R. J. Furstoss, *J. Org. Chem.* 1999, **64**, 6112.

4 B. T. Cho, W. K. Yang and O. K. Choi *J. Chem Soc., Perkin Trans. 1* 2001, 1204.

5 K. Matsumoto, T. Oguma and T. Katsuki, *Angew. Chem. Int. Ed.* 2009, **121**, 7568.

6 L. F. Tietze, H. Geissler, J. A. Gewert and U. Jakobi, *Synlett* 1994, 511.

7 D. S. Bose, A. V. N. Reddy and B. Srikanth, *Synthesis* 2008, **15**, 2323.

8 M. Tokunaga, J. F. Larrow, F. Kakiuchi and E. N. Jacobsen, *Science* 1997, **277**, 936.

9 R. F. Campbell, K. Fitzpatrick, T. Inghardt, O. Karlsson, K. Nilsson, J. E. Reillya and L. Yeta, *Tetrahedron Lett.* 2003, **44**, 5477.

10 (a) R. Truxa and M. Suchoparek, *Makromol. Chem.* 1990, **191**, 1931 (b) M. Inoue, E. Nakayama, Y. Nakamura, S. Rengakuji and K. Nishibe, *Bull. Chem. Soc. Jpn.* 1991, **64**, 3442

11 V. Genzel, A. Archelas, Q. B. Broxterman, B. Schulze and R. Furstoss, *J. Org. Chem.* 2001, **66**, 538.

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