Electronic Supporting Information

The Generation and Trapping of Enantiopure Bromonium Ions

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ESI Available:

i) Full experimental details and characterising data for compounds **4** and **6-24**;

ii) Copies of ^{1}H and ^{13}C NMR spectra for **13-22**;

iii) Copies of ^{1}H NMR spectra for Mosher ester derivatives of **6**, **7**, **9**, **10**, **23** and **24**;

iv) Chiral HPLC analysis of **11&12**;

v) Optical rotation measurements, NMR integration and ee calculations for **13** and **14**;

vi) Copies of ^{13}C NMR spectra showing halide-induced isotopic shifts for **4**, **13**, **14**, **23** and **24**;

vii) X-ray crystallographic details for **4** and **11.**

Full experimental details and characterising data for compounds **4** and **6-24**

General Methods: Melting points were recorded on a Reichart-Thermovar melting point apparatus and are uncorrected. Fourier transform infra-red (IR) spectra were recorded through Diffuse Reference Infra-red Fourier Transform Spectroscopy (DRIFTS) or as thin films on NaCl plates using a Mattson 500 FT IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz or 100 MHz on a Bruker Avance 400 spectrometer respectively. NMR samples were run in the indicated solvents and were referenced internally. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. The following abbreviations are used for the multiplicity of NMR signals: br = broad, s = singlet, d = doublet, t = triplet, quint. = quintet, sext. = sextet, m = multiplet. Low Resolution Mass Spectra (MS) [EI, CI] and High Resolution Mass Spectra (HRMS) were recorded by the Imperial College Department of Chemistry Mass Spectroscopy Service. Elemental analyses were carried out by the University of North London Analytical Service.

Experimental procedures: Concentrated refers to removal of solvent under reduced pressure on a rotary evaporator. Analytical thin-layer chromatography (TLC) was carried out on silica gel $F_{254/366}$ 60 Å plates with visualisation using UV light (254 nm), cerium molybdenum solution, or potassium permanganate as appropriate. Chromatography was performed using BDH 33-70 μm grade silica gel.

Reagents: CH_2Cl_2 was distilled from CaH_2. All other reagents were used as received.

(±)-2-Bromo-1-chloro-1-phenylethane (4). (±)-2-Bromo-2-phenylethanol (**1**) (50 mg, 0.25 mmol) was stirred at 65 °C in neat thionyl chloride (25-30 eq.) for 1.5-5.5 h. The reaction mixture was allowed to cool and concentrated. The residue was taken up in dichloromethane and washed with a saturated aqueous solution of sodium hydrogen carbonate. The aqueous phase was re-extracted with dichloromethane and the combined organic phases were washed with water, dried ($MgSO_4$), filtered and concentrated. The crude product was purified by column chromatography (petrol) to afford (±)-2-bromo-1-chloro-1-phenylethane **4** (38 mg, 69%) as colourless low melting needles with spectral data consistent with literature (reference 9 in the main manuscript): m.p. 21-22.5 °C; R_f = 0.25 (petrol); FT IR (NaCl) ν_{max} 3065, 3034, 2960, 1953 (w), 1884 (w), 1805 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 5H, Ar-*H*), 5.09 (dd, J = 8.8, 6.4 Hz, 1H, PhC*H*Cl), 3.94 (dd, J^3 = 6.4 Hz, J^2 = 10.4 Hz, 1H, C*H*H'Br), 3.86 (dd, J^3 = 8.8 Hz, J^2 = 10.4

Hz, 1H, CH*H'*Br) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 129.2, 128.8, 127.4, 61.3, 36.0 ppm; MS (EI^+) 218/220/222 ($M^{+\cdot}$), 125/127 ($PhCHCl^{+\cdot}$); HRMS calcd for ($M^{+\cdot}$) $C_8H_8{}^{35}Cl\ {}^{79}Br$ 217.9498, $C_8H_8{}^{35}Cl^{81}Br$ 219.9477, $C_8H_8{}^{37}Cl^{79}Br$ 219.9468 and $C_8H_8{}^{37}Cl^{81}Br$ 221.9448, found 217.9494, 219.9474 and 221.9444.

(1*R*,2*S*)-1-Bromo-1-phenylpropan-2-ol (6) and (1*S*,2*S*)-1-Bromo-1-phenylpropan-2-ol (7). To a stirred solution of (1*S*, 2*S*)-1-phenylpropylene oxide (**5**) (1.05 mL, 7.75 mmol) in chloroform (20 mL) at -10 °C was added a cooled (-10 °C) 48% aqueous solution of hydrobromic acid (20 mL). The biphasic mixture was stirred for 35 mins, diluted with water (300 mL) and extracted with dichloromethane (2 × 150 mL). The combined organic extracts were washed with water (200 mL), dried ($MgSO_4$), filtered and concentrated. The crude product was purified by flash column chromatography (4:1, dichloromethane:petrol) to afford the title compounds **6** and **7** (1.47 g, 88%) in an inseparable 75:25 mixture as a colourless oil: R_f = 0.36 (4:1, dichloromethane:petrol); $[\alpha]_D^{27}$ -43.4 (*c* 2.2, CH_2Cl_2); FT IR (NaCl) υ_{max} 3409 (br), 3092, 3030, 2978, 2932, 2897, 1953(w), 1882(w), 1807(w), 1710(w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1*R*,2*S*) 7.50-7.48 (m, 2H, Ar-*H*), 7.43-7.33 (m, 3H, Ar-*H*), 4.90 (d, *J* = 6.4 Hz, 1H, PhC*H*), 4.29-4.19 (m, 1H, C*H*(OH)CH_3), 2.04 (br s, 1H, O*H*), 1.38 (d, *J* = 6.0 Hz, 3H, C*H*$_3$), (1*S*, 2*S*) 7.43-7.33 (m, 5H, Ar-H), 4.89 (d, *J* = 8.4 Hz, 1H, PhC*H*), 4.29-4.19 (m, 1H, C*H*(OH)CH_3), 2.04 (br s, 1H, O*H*), 1.13 (d, *J* = 6.4 Hz, 3H, C*H*$_3$) ppm; ^{13}C NMR (100MHz, $CDCl_3$) δ (1*R*, 2*S*) 138.2, 128.8, 128.8, 128.7, 71.6, 60.8, 20.1, (1*S*, 2*S*) 139.1, 128.8, 128.8, 128.0, 71.6, 65.1, 19.7 ppm; ; GCMS (EI^+) 12.98 min; (1*S*, 2*S*)-diastereomer, 170/172 ($PhCHBr+H^+$), 214/216 (M^+), 13.38 min; (1*R*, 2*S*)-diastereomer, 170/172 ($PhCHBr+H^+$), 214/216 (M^+); HRMS *m/z* calcd for (M^+) $C_9H_{11}O^{79}Br$ 213.9993 and $C_9H_{11}O^{81}Br$ 215.9973, found 213.9989 and 215.9971. The fragmentation pattern in the MS clearly defines both these compounds as benzylic bromides. A mixture of racemic compounds were prepared in identical fashion from (±)-1-phenylpropylene oxide.

(*R*)-1,2-Oxiranyldodecane (8). Following the method of Jacobsen (reference 15 in the main manuscript), to a stirred solution of (*R,R*)-(-)-*N,N*'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) (33 mg, 0.05 mmol) in toluene (1 mL) was added acetic acid (32 mg, 0.55 mmol), and the solution was allowed to stir open to the air for 1 h. The volatiles were then removed *in vacuo*, and the residue was dissolved in propan-2-ol (2 mL). Racemic 1,2-oxiranyldodecane (2 g, 10.88 mmol) was added, the solution was cooled to 0°C, and then water (196 mg, 10.88 mmol) in propan-2-ol (0.4 mL) was added drop-wise. The solution was allowed to stir for 24 h at r.t. after which time the mixture was adsorbed on to silica gel, and purified by

silica gel column chromatography (100% petroleum spirits to 2:1 petroleum spirits/diethyl ether) to give **8** (891 mg, 44% yield) as a colourless oil. Spectra is identical to that of racemate. $[\alpha]_D^{23}$ +6.0 (*c* 0.3, CH_2Cl_2); lit. (ref. 16 in main manuscript) $[\alpha]_D$ +6.92 (*c* 1.04, $CHCl_3$).

(*S*)-2-Bromododecan-1-ol (9) and (*R*)-1-Bromododecan-2-ol (10). To a stirred solution of epoxide **9** (810 g, 4.4 mmol) in chloroform (30 mL) at -10°C was added HBr as a 48% solution (1.4 mL, 17.6 mmol) drop-wise. The reaction was stirred for 2 h, and was allowed to slowly warm to r.t. The reaction mixture was diluted with water (20 mL), the organic phase was separated, and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over magnesium sulfate, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (5:1 petroleum spirits/diethyl ether) to give first **10** (693 mg, 60%) as a colourless oil R*f* = 0.35 (3:1 petroleum spirits/diethyl ether): $[\alpha]_D^{23}$ -2.7 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90–3.72 (m, 1H), 3.58 (dd, *J* = 10.3, 3.3 Hz, 1H), 3.40 (dd, *J* = 10.3, 7.2 Hz, 1H), 2.12 (bd, *J* = 5.0 Hz, 1H), 1.65–1.20 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.1, 40.8, 35.1, 31.9, 29.6 (2C), 29.5, 29.3, 25.6, 22.7, 14.1; and second **9** (281 mg, 24%) as a colourless oil R*f* = 0.30 (3:1 petroleum spirits/diethyl ether): $[\alpha]_D^{23}$ -28.3 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28–4.12 (m, 1H), 3.96–3.75 (m, 2H), 2.10–1.95 (m, 1H), 1.90–1.80 (m, 2H), 1.75–1.20 (m, 16H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.3, 60.3, 34.9, 31.9, 29.6, 29.4, 29.3 (2C), 29.0, 27.5, 22.7, 14.1. The racemic compounds were prepared by an identical procedure from racemic epoxide.

Tosylates 15 and 16. (1*R*, 2*S*) and (1*S*, 2*S*)-1-Bromo-1-phenylpropan-2-ols (**6** and **7**) (100 mg, 0.47 mmol), as a 73:27 mixture of the diastereomers, were stirred with DMAP (114 mg, 0.93 mmol) in dichloromethane (4 mL) under an inert atmosphere of nitrogen. The solution was cooled to 0 ºC and tosyl chloride (133 mg, 0.70 mmol) was added. The reaction mixture was allowed to gradually warm to RT and stirred for 19 h. The mixture was diluted with dichloromethane (20 mL), washed with brine (20 mL), dried (Na_2SO_4), filtered and concentrated. The crude product was purified by flash column chromatography (1:1, dichloromethane:petrol) to afford the desired products (161 mg, 94%) as a colourless amorphous solid in a 72:28 inseparable mixture of the (1*R*, 2*S*) and (1*S*, 2*S*) diastereomers **15** and **16** respectively: R*f* = 0.29 (1:1, dichloromethane/petrol); $[\alpha]_D^{23}$ -15.5 (*c* 1.0, CH_2Cl_2); FT IR (NaCl) υ_{max} 3064, 3032, 2990, 2938, 2873, 1920 (w), 1809 (w),1362, 1177 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1*R*, 2*S*) 7.58 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.36-7.24 (m, 7H, Ar-*H*), 4.94-4.89 (m, 2H, PhC*H*Br and C*H*CH_3), 2.45 (s,

3H, Ar-C*H*$_3$), 1.55 (d, *J* = 5.6 Hz, 3H, CH(OSO$_2$Ar)C*H*$_3$), (1*S*, 2*S*) 7.83 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.36-7.24 (m, 7H, Ar-*H*), 5.02 (quint., *J* = 6.4 Hz, 1H, C*H*CH$_3$), 4.94-4.89 (m, 1H, PhC*H*Br), 2.47 (s, 3H, Ar-C*H3*), 1.29 (d, *J* = 6.4 Hz, 3H, CHC*H*$_3$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ (1*R*, 2*S*) 144.7, 137.2, 133.7, 129.7, 128.7, 128.6, 128.5, 127.7, 80.8, 56.0, 21.7, 18.9, (1*S*, 2*S*) 144.9, 136.8, 133.8, 129.8, 128.9, 128.6, 128.6, 128.0, 81.1, 55.1, 21.7, 18.6 ppm; MS (CI+) 386/388 (M+NH$_4^+$); HRMS calcd for (M+ NH$_4^+$) $C_{16}H_{21}NO_3{}^{79}BrS$ 386.0426 and $C_{16}H_{21}NO_3{}^{81}BrS$ 388.0405, found 386.042 8 and 388.0407; Anal. calcd for $C_{16}H_{17}O_3BrS$: C, 52.04; H, 4.64; found: C, 52.13; H, 4.62.

Tosylate 17. To as stirred solution of bromhydrin **9** (200 mg, 0.76 mmol) in dichloromethane (15 mL) at 0°C was added DMAP, followed by *p*-toluenesulfonyl chloride (173 mg, 0.91 mmol). The reaction mixture was stirred at r.t. for 16 h, then diluted with dichloromethane (10 mL), and the organic phase was washed with brine, dried over magnesium sulfate, concentrated and the residue was purified by silica gel column chromatography (9:1 petroleum spirit/diethyl ether) to give primary tosylate **17** (250 mg, 79% yield) as a colourless oil: R*f* = 0.65 (9:1 petroleum spirits/diethyl ether); $[\alpha]_D^{23}$ -13.7 (*c* 0.3, CH_2Cl_2); FT IR (NaCl) υ_{max} 2926, 2854, 1597, 1461, 1368, 1177, 961 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 4.26 (dd, *J* = 10.4, 5.7 Hz, 1H), 4.16 (dd, *J* = 10.4, 7.2 Hz, 1H), 4.09–4.01 (m, 1H), 2.48 (s, 3H), 1.96–1.86 (m, 1H), 1.71 (m, 1H), 1.55–1.21 (m, 16H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.2, 132.7, 130.0, 128.0, 72.2, 49.9, 34.6, 31.9, 29.6, 29.5, 29.4, 29.3, 28.8, 26.8, 22.7, 21.7, 14.1; MS (CI+) 436/438 (M+NH$_4^+$); HRMS calcd for (M+ NH$_4^+$) $C_{19}H_{35}NO_3{}^{79}BrS$ 436.1521 and $C_{16}H_{21}NO_3{}^{81}BrS$ 438.1501, found 436.1526 and 438.1508

Tosylate 18. To as stirred solution of bromohydrin **10** (300 mg, 1.1 mmol) in dichloromethane (20 mL) at 0°C was added DMAP (276 mg, 2.3 mmol), followed by *p*-toluenesulfonyl chloride (260 mg, 1.4 mmol). The reaction mixture was stirred at r.t. for 16 h, then diluted with dichloromethane (10 mL), and the organic phase was washed with brine, dried over magnesium sulfate, concentrated, and the residue was purified by silica gel column chromatography (9:1 petroleum spirit/diethyl ether) to give secondary tosylate **18** (412 mg, 87% yield) as a colourless oil: R*f* = 0.65 (9:1 petroleum spirits/diethyl ether); $[\alpha]_D^{23}$ +21.7 (*c* 0.3, CH_2Cl_2); FT IR (NaCl) υ_{max} 2923, 2854, 1369, 1176, 1096 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 4.67–4.60 (m, 1H), 3.54–3.45 (m, 2H), 2.48 (s, 3H), 1.82–1.70 (m, 2H), 1.35–1.16 (m, 16H), 0.91 (t, *J* = 6.9 Hz, 3H),; ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.0, 133.8, 129.8, 127.9, 80.6, 33.2, 32.7, 31.9, 29.6, 29.5, 29.3, 29.0, 24.4, 22.7, 21.7, 14.1; MS (CI+)

436/438 ($M+NH_4^+$); HRMS calcd for ($M+NH_4^+$) $C_{19}H_{35}NO_3{}^{79}BrS$ 436.1521 and $C_{16}H_{21}NO_3{}^{81}BrS$ 438.1501, found 436.1525 and 438.1509

Benzenesulphonates 19 and 20. (1*R*, 2*S*) and (1*S*, 2*S*)-1-Bromo-1-phenylpropan-2-ols (**6** and **7**) (100 mg, 0.47 mmol), as a 75:25 mixture of diastereomers, were stirred with DMAP (85 mg, 0.70 mmol) in dichloromethane (3 mL) under an inert atmosphere of nitrogen. The solution was cooled to 0ºC and a solution of 2-(2-methoxyethoxy)ethyl 2-(chlorosulfonyl)benzoate (180 mg, 0.56 mmol) in dichloromethane (2 mL) was added. The reaction mixture was allowed to gradually warm to RT and stirred for 20 h. The mixture was concentrated and the resulting crude oil was purified by flash column chromatography (3:2, ethyl acetate:petrol) to yield an inseparable mixture of the diastereomeric benzene sulphonates (1*R*, 2*S*)-**19** and (1*S*, 2*S*)-**20** (167 mg, 72%) as a colourless gum in a 70:30 ratio: R*f* = 0.48 (3:2, ethyl acetate/petrol); $[\alpha]_D^{24}$ -7.3 (*c* 2.6, CH_2Cl_2); FT IR (NaCl) υ_{max} 3065, 3032, 2880, 1959(w), 1736, 1367 (SO_2), 1185 (SO_2) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1*R*, 2*S*) 7.78 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.70-7.21 (m, 8H, Ar-*H*), 5.15 (quint., *J* = 6.2 Hz, 1H,C*H*(OSO_2Ar)CH_3), 5.06 (d, *J* = 6.0 Hz, 1H, PhC*H*Br), 4.58-4.54 (m, 2H, C(O)OC*H*$_2$), 3.87-3.85 (m, 2H, C*H*$_2$O), 3.71-3.67 (m, 2H, C*H*$_2$O), 3.59-3.56 (m, 2H, C*H*$_2$O), 3.40 (s, 3H, OC*H*$_3$) 1.58 (d, *J* = 6.4 Hz, 3H, C*H*$_3$), (1*S*, 2*S*) 8.04 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.70-7.21 (m, 8H, Ar-*H*), 5.26 (quint., *J* = 6.5 Hz, 1H, C*H*(OSO_2Ar)CH_3), 5.02 (d, *J* = 6.8 Hz, 1H,PhC*H*Br), 4.58-4.54 (m, 2H, C(O)OC*H*$_2$), 3.87-3.85 (m, 2H, C*H*$_2$O), 3.71-3.67 (m, 2H, C*H*$_2$O), 3.59-3.56 (m, 2H, C*H2*O), 3.40 (s, 3H, OC*H*$_3$) 1.31 (d, *J* = 6.4 Hz, 3H, C*H*$_3$) ppm; ^{13}C NMR (100MHz, CDCl3) (1*R*, 2*S*); δ 166.2, 137.1, 134.8, 133.3, 132.9, 130.7, 129.3, 128.6, 128.5 128.4, 82.1, 71.9, 70.5, 68.7, 65.3, 59.0, 56.1, 18.8 ppm; (1*S*, 2*S*); 166.8, 136.8, 134.8, 133.5, 133.2, 130.7, 129.7, 129.5, 129.3, 128.9, 82.3, 71.9, 70.4, 68.7, 65.3, 59.0, 54.9, 18.5 ppm; MS (ES^+) 523/525 ($M+Na^+$); HRMS calcd for ($M+Na^+$) $C_{21}H_{25}O_7S^{79}BrNa$ 523.0402 and $C_{21}H_{25}O_7S^{81}BrNa$ 525.0382, found 523.0381 and 525.0365; Anal. calcd for $C_{21}H_{25}O_7SBr$: C, 50.31; H, 5.03; found: C, 50.43; H, 5.09.

Benzenesulphonate 21. To a solution of bromohydrin **9** (60 mg, 0.23 mmol) in dichloromethane (4 mL) at 0°C was added DMAP (55 mg, 0.45 mmol), and a solution of 2-(2-methoxyethoxy)ethyl 2-(chlorosulfonyl)benzoate (95 mg, 0.29 mmol) in dichloromethane (2 mL). The reaction mixture was stirred for 24 h, concentrated, and the residue was purified by silica gel column chromatography (1:1 petroleum spirit/diethyl ether) to give primary benzenesulphonate **21** (91 mg, 73% yield) as a colourless oil. R*f* = 0.15 (4:1 petroleum spirits/diethyl ether); $[\alpha]_D^{21}$ -14.7 (*c* 0.3, CH_2Cl_2); FT IR (NaCl) υ_{max} 2925, 2854, 1739, 1466, 1371, 1292, 1260, 1187; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 3.7 Hz, 2H), 7.68 (td, *J* = 8.7, 4.1 Hz, 1H), 4.55 (dd, *J* =5.8, 4.1 Hz, 2H), 4.42 (dd, *J* = 10.7, 5.8 Hz, 1H), 4.32 (dd, *J* = 10.7, 7.1 Hz, 1H), 4.15–4.07 (m, 1H), 3.86 (dd, *J* = 5.6, 4.2 Hz, 2H), 3.69 (dd, *J* = 5.6, 3.6 Hz, 2H), 3.57 (dd, *J* = 5.6, 3.6 Hz, 2H), 3.40 (s, 3H), 2.01–1.90 (m, 1H), 1.74 (m, 1H), 1.57–1.46 (m, 1H), 1.45–1.19 (m, 15H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 133.8, 133.7, 133.3, 130.9, 129.9, 129.7, 73.1, 71.9, 70.5, 69.7, 65.4, 59.1, 50.0, 34.6, 31.9, 29.6, 29.5, 29.4, 29.3, 28.8, 26.8, 22.7, 14.1; MS (ESI+) 573/575 ($M+Na^+$); HRMS calcd for ($M+Na^+$) $C_{24}H_{39}O_7{}^{79}BrNaS$ 573.1498 and $C_{24}H_{39}O_7{}^{81}BrNaS$ 575.1477, found 573.1503 and 575.1478

Benzenesulphonate 22. To a solution of bromohydrin **10** (300 mg, 1.13 mmol) in dichloromethane (15 mL) at 0°C was added DMAP (276 mg, 2.26 mmol), and a solution of 2-(2-methoxyethoxy)ethyl 2-(chlorosulfonyl)benzoate (548 mg, 1.69 mmol) in dichloromethane (5 mL). After stirring for 24 h the mixture was concentrated and the residue was purified by silica gel column chromatography (1:1 petroleum spirit/diethyl ether) to give secondary benzenesulphonate **22** (580 mg, 93% yield) as a colourless oil. R*f* = 0.15 (4:1 petroleum spirits/diethyl ether); $[\alpha]_D^{24}$ +11.0 (*c* 0.3, CH_2Cl_2); FT IR (NaCl) υ_{max} 2925, 2855, 1738, 1459, 1370, 1293, 1259, 1184, 1112; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.03 (m, 1H), 7.75–7.60 (m, 3H), 4.90–4.78 (m, 1H), 4.60–4.52 (m, 2H), 3.90–3.83 (m, 2H), 3.70–3.67 (m, 2H), 3.56–3.45 (m, 4H), 2.36 (s, 3H), 1.90–1.75 (m, 2H), 1.40–1.20 (m, 16H), 0.88 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 134.7, 133.6, 133.2, 130.8, 129.8, 129.5, 81.8, 71.9, 70.5, 68.7, 65.4, 59.0, 33.2, 32.7, 31.9, 29.5, 29.4, 29.3, 29.0, 24.3, 22.7, 14.1; MS (ESI+) 573/575 ($M+Na^+$); HRMS calcd for ($M+Na^+$) $C_{24}H_{39}O_7{}^{79}BrNaS$ 573.1498 and $C_{24}H_{39}O_7{}^{81}BrNaS$ 575.1477, found 573.1495 and 575.1470.

(*S*)-2-Chlorododecan-1-ol (23) and (*R*)-1-Chlorododecan-2-ol (24). To a stirred solution of epoxide **8** (600 mg, 3.26 mmol) in chloroform (20 mL) at -10°C was added HCl as a 37% solution (1.8 mL, 21.76 mmol) drop-wise. The reaction mixture was stirred for 2 h, and was allowed to slowly warm to approximately 0°C. The reaction mixture was diluted with water (100 mL), the organic phase was separated, and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over magnesium sulfate, concentrated, and the residue was purified by silica gel column chromatography (5:1 petroleum spirits/diethyl ether) to give first **24** (431 mg, 60%) as a colourless oil: R*f* = 0.35 (3:1 petroleum spirits/diethyl ether) $[\alpha]_D^{22}$ -2.0 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87–3.79 (m, 1H), 3.67 (dd, *J* = 11.3, 2.9 Hz, 1H), 3.51 (dd, *J* = 11.3, 7.2 Hz, 1H), 2.15 (d, *J* = 4.9 Hz, 1H), 1.61–1.24 (m, 18H), 0.91

(t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.5, 50.6, 34.2, 31.9, 29.6 (2C), 29.5 (2C), 29.3, 25.5, 22.7, 14.1; and second **23** (180 mg, 25%) as a colourless oil: Data for **23**: R*f* = 0.30 (3:1 petroleum spirits/diethyl ether) $[\alpha]_D^{22}$ -25.7 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08–4.01 (m, 1H), 3.81 (ddd, *J* = 11.9, 8.1, 3.9 Hz, 1H), 3.68 (ddd, *J* = 11.9, 7.1, 5.3 Hz, 1H), 2.04–1.98 (m, 1H), 1.82–1.71 (m, 1H), 1.62–1.22 (m, 17H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.1, 65.5, 34.3, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 26.4, 22.7, 14.1. The racemic compounds were prepared by an identical procedure.

General procedure A for the rearrangement of bromohydrins with thionyl chloride. The bromohydrin (1 eq.) was stirred at 65 °C in neat thionyl chloride (25-30 eq.) for 1.5-5.5 h. The reaction mixture was allowed to cool and concentrated. The residue was taken up in dichloromethane and washed with a saturated aqueous solution of sodium hydrogen carbonate. The aqueous phase was re-extracted with dichloromethane and the combined organic phases were washed with water, dried (MgSO4), filtered and concentrated. The crude product was subjected to flash column chromatography (petrol).

General procedure B for the rearrangement of sulphonates with $TiCl_4$. To a dichloromethane solution of sulphonate (0.1 mmol), cooled to -78 ºC, was added $TiCl_4$ (22 μL, 0.2 mmol). The resulting bright yellow mixture was allowed to gradually warm to RT and stirred for 24 h. The reaction was quenched with water (10 mL) and extracted with dichloromethane (10 mL). The organic phase was passed through a silica gel plug and concentrated. See Table 1 for the collected results on substrates **17**, **18**, **21** and **22**.

(1*S*,2*R*)-2-Bromo-1-chloro-1-phenylpropane (11) and (1*R*, 2*R*)- 2-Bromo-1-chloro-1-phenylpropane (12). Following general procedure A, (1*R*, 2*S*) and (1*S*, 2*S*)-1-bromo-1-phenylpropan-2-ols (**6** and **7**) (100 mg, 0.47 mmol), as a 73:23 mixture of the diastereomers afforded inseparable diastereomers **11** and **12** (59 mg, 97%) as a colourless oil in a 76:24 ratio. R*f* = 0.33 (petrol); FT IR (NaCl) υ_{max} 3064, 3033, 2982, 2932, 2868, 1952 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1*S*, 2*R*) 7.47-7.36 (m, 5H, Ar-*H*), 5.02 (d, *J* = 8.4 Hz, 1H, PhC*H*Cl), 4.57-4.46 (m, 1H, C*H*BrCH$_3$), 1.96 (d, *J* = 6.4 Hz, 1H, C*H*$_3$), (1*R*, 2*R*) 7.47-7.36 (m, 5H, Ar-*H*), 5.12 (d, *J* = 6.0 Hz, 1H, PhC*H*Cl), 4.57-4.46 (m, 1H, C*H*BrCH$_3$),1.69 (d, *J* = 6.8 Hz, 1H, C*H*$_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ (1*S*, 2*R*) 139.5, 128.9, 128.6, 127.6, 51.7, 23.6, (1*R*, 2*R*) 137.2, 128.4, 128.2, 127.6, 67.5, 53.0, 22.4 ppm; GCMS (EI$^+$) 13.67 min; (1*S*, 2*R*)-diastereomer, 125/127 (PhCHCl$^{+\cdot}$), 232/234/236 (M$^{+\cdot}$), 14.17 min; (1*R*, 2*R*)-diastereomer, 125/127 (PhCHCl$^{+\cdot}$),

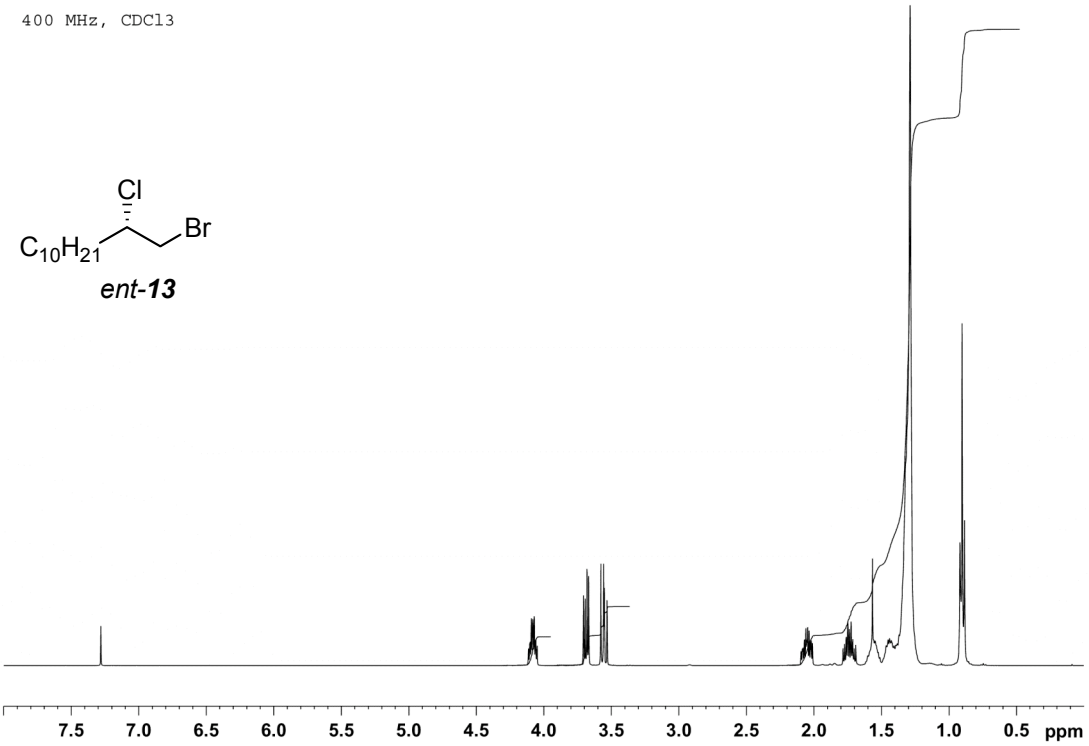
232/234/236 ($M^{+\cdot}$); HRMS calcd for (M^+) $C_9H_{10}{}^{35}Cl^{79}Br$ 231.9654, $C_9H_{10}{}^{37}Cl^{79}Br$ 233.9625, $C_9H_{10}{}^{35}Cl^{81}Br$ 233.9634 and $C_9H_{10}{}^{37}Cl^{81}Br$ 235.9604, found 231.9650, 233.9629 and 235.9612. The fragmentation pattern in the MS clearly defines both these compounds as benzylic chlorides. A racemic sample was prepared from racemic bromohydrin for chiral HPLC analysis (*vide infra*): HPLC (1:1,water:acetonitrile+0.05% TFA); Chiralcel OJ-RH: 1 mL/min; 240 nm, t_R (1*S*,2*S*) 19.71 min, t_R (1*R*,2*R*) 22.68 min, t_R (1*S*,2*R*) 23.65 min, t_R (1*R*,2*S*) 27.39 min. Following general procedure B, tosylates **15** and **16** (50 mg), as a 70:30 mixture of the diastereoisomers, afforded inseparable diastereomers **11** and **12** (21 mg, 100%) as a colourless oil in a 67:33 ratio. Following general procedure B, benzenesulphonates **19** and **20** (50 mg), as a 65:35 mixture of the diastereoisomers, afforded inseparable diastereomers **11** and **12** (21 mg, 89%) as a colourless oil in a 86:14 ratio.

(*S*)-1-Bromo-2-chlorododecane (*ent*-13) To a stirred solution of **23** (45 mg, 0.2 mmol) in dichloromethane (2 mL) was added carbon tetrabromide (81 mg, 0.25 mmol). The solution was cooled to 0°C, and triphenylphosphine (64 mg, 0.25 mmol) was added. The reaction mixture was allowed to warm to r.t. and was stirred for 24 h. The mixture was concentrated, and the residue was purified by silica gel column chromatography (petroleum spirits) to give *ent*-**13** (50 mg, 87% yield) as a colourless oil. R*f* = 0.80 (petroleum spirits) $[\alpha]_D^{24}$ -29.0 (*c* 0.3, CH_2Cl_2); FT IR (NaCl) υ_{max} 2925, 2854, 1464; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12–4.04 (m, 1H), 3.69 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.55 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.10–2.01 (m, 1H), 1.79–1.68 (m, 1H), 1.62–1.51 (m, 1H), 1.50–1.24 (m, 15H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.9, 36.5, 35.8, 31.9, 29.6, 29.5, 29.4, 29.3, 28.9, 25.8, 22.7, 14.1; MS (ESI+) 281/283 ($M–H^+$); HRMS calcd for ($M–H^+$) $C_{24}H_{39}O_7{}^{79}BrNaS$ 281.0672 and $C_{24}H_{39}O_7{}^{81}BrNaS$ 283.0651, found 281.0676 and 283.0651.

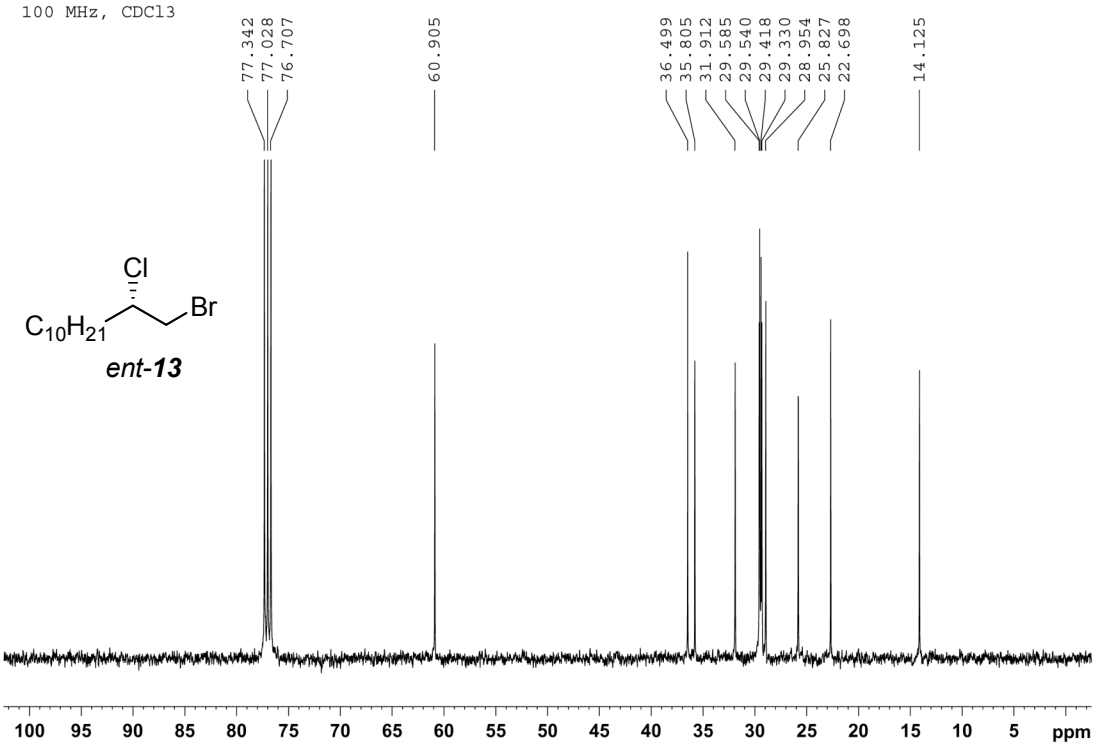
(*S*)-2-Bromo-1-chlorododecane (14). To a stirred solution of **24** (110 mg, 0.5 mmol) in dichloromethane (5 mL) was added carbon tetrabromide (198 mg, 0.6 mmol). The solution was cooled to 0°C, and triphenylphosphine (157 mg, 0.6 mmol) was added. The reaction mixture was allowed to warm to r.t. and was stirred for 24 h. The mixture was concentrated, and the residue was purified by silica gel column chromatography (petroleum spirits) to give **14** (140 mg, 99% yield) as a colourless oil. R*f* = 0.80 (petroleum spirits); $[\alpha]_D^{24}$ -32.0 (*c* 0.3, CH_2Cl_2); FT IR (NaCl) υ_{max} 2925, 2854, 1464 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17–4.09 (m, 1H), 3.93 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.75 (dd, *J* = 11.2, 8.7 Hz, 1H), 2.15–2.05 (m, 1H), 1.80 (m, 1H), 1.64–1.53 (m, 1H), 1.51–1.24 (m, 15H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 48.3,

35.4, 31.9, 29.6, 29.5, 29.4, 29.3, 28.9, 26.8, 22.7, 14.1; MS (ESI+) 281/283 ($M–H^+$); HRMS calcd for ($M–H^+$) $C_{24}H_{39}O_7{}^{79}BrNaS$ 281.0672 and $C_{24}H_{39}O_7{}^{81}BrNaS$ 283.0651, found 281.0674 and 283.0648.

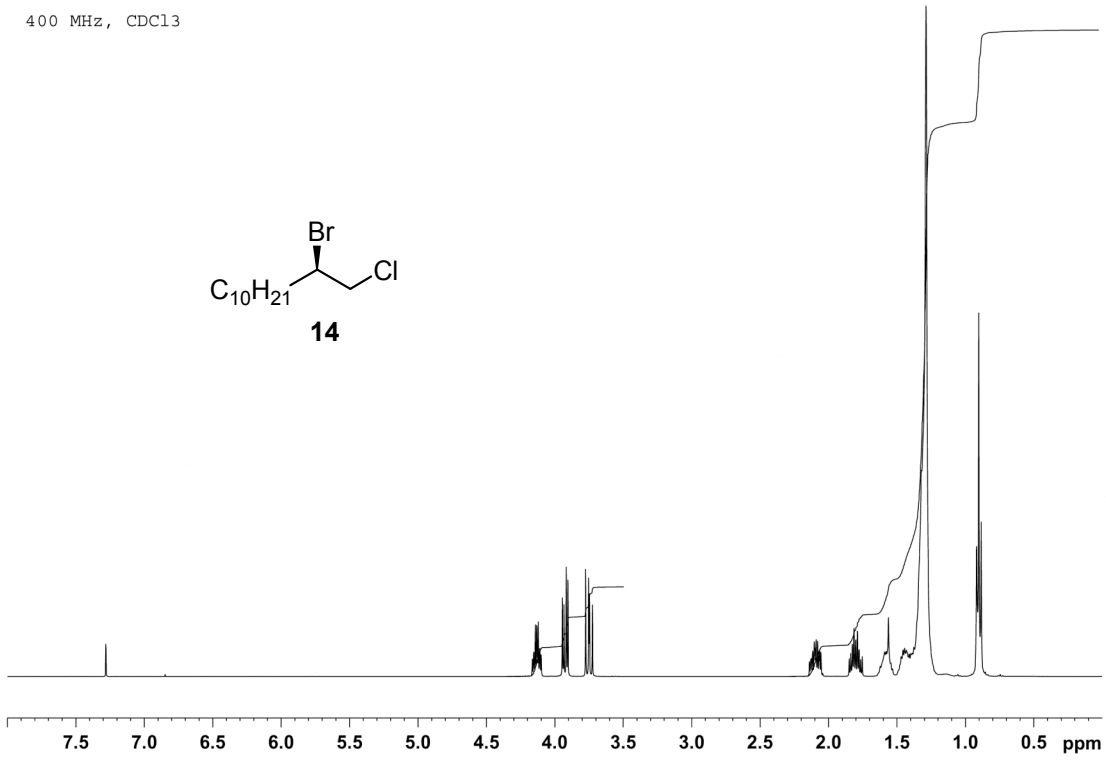
Copies of ^{1}H and ^{13}C NMR spectra for **13-22**



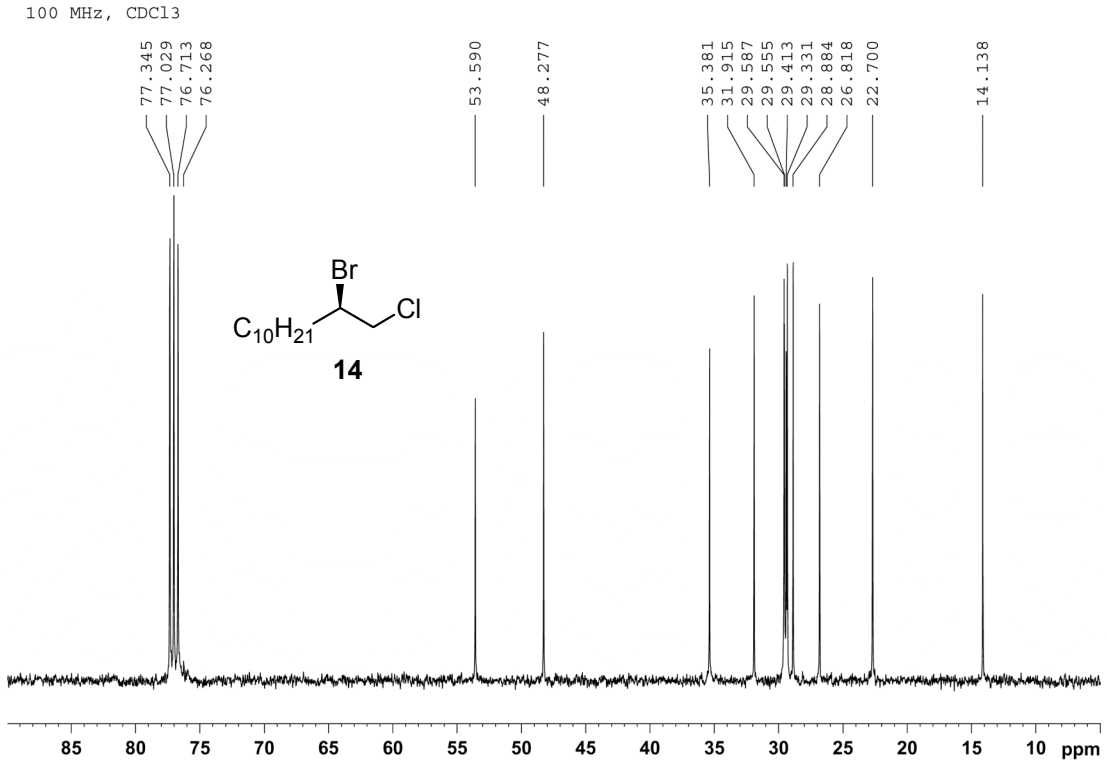
^{1}H NMR spectrum of bromochloride *ent*-**13**



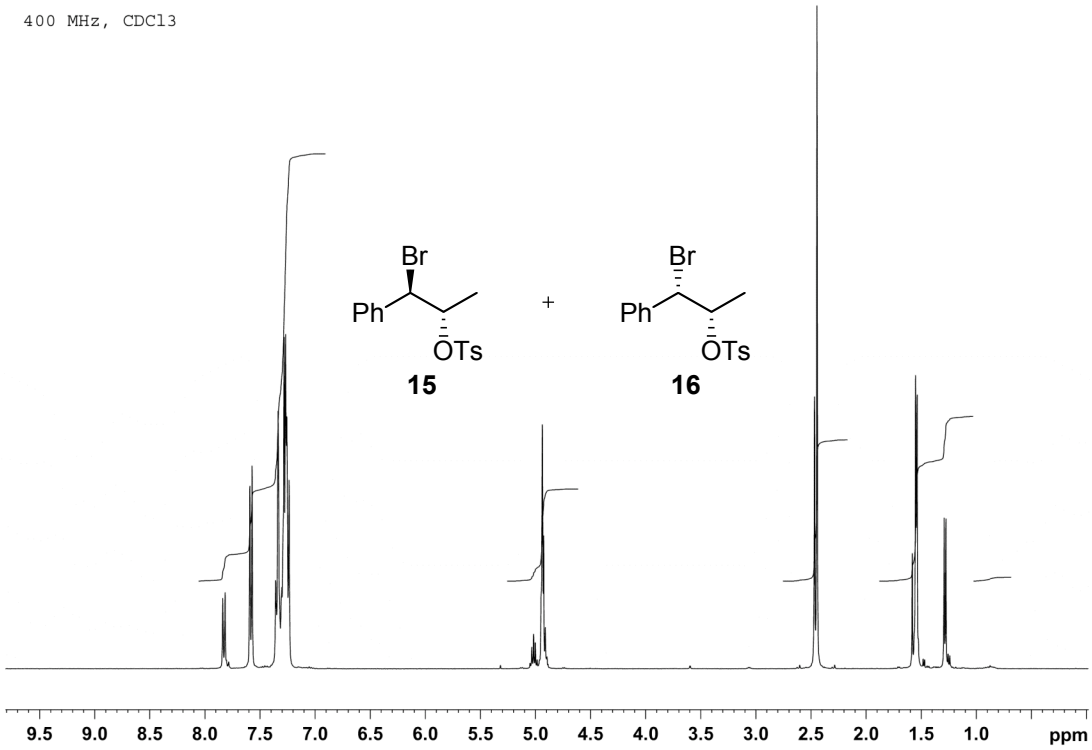
^{13}C NMR spectrum of bromochloride *ent*-**13**



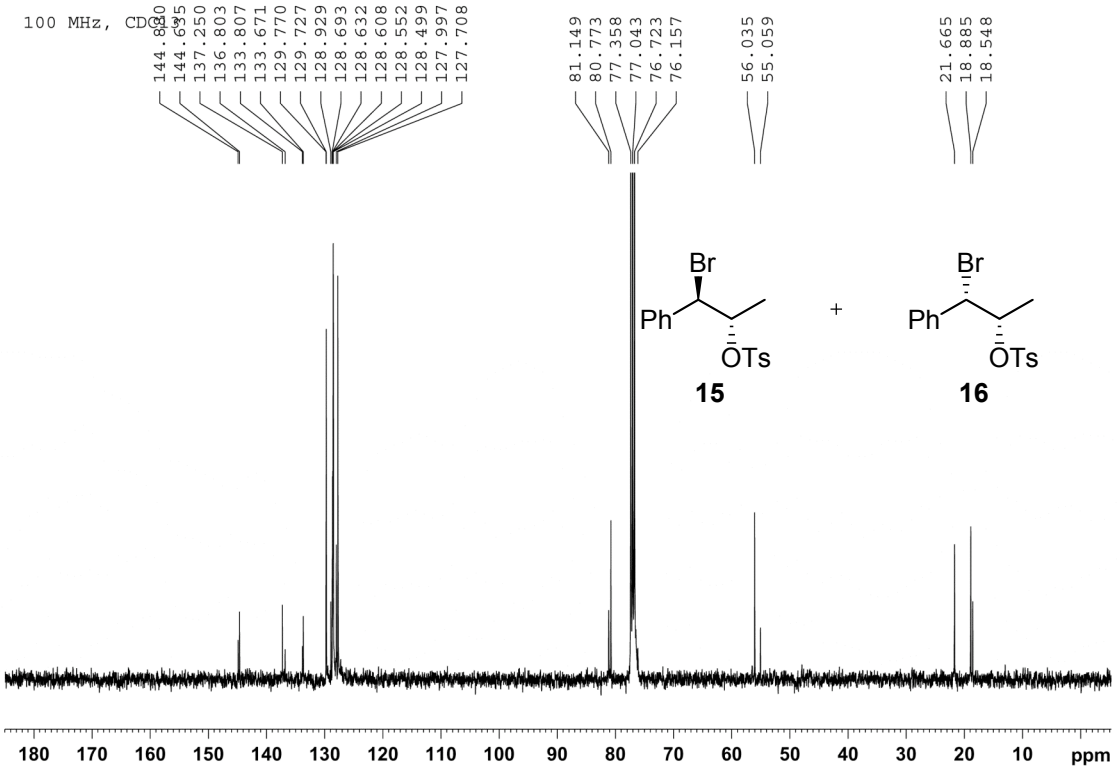
^{1}H NMR spectrum of bromochloride **14**



^{13}C NMR spectrum of bromochloride **14**



^{1}H NMR spectrum of tosylates **15** and **16**



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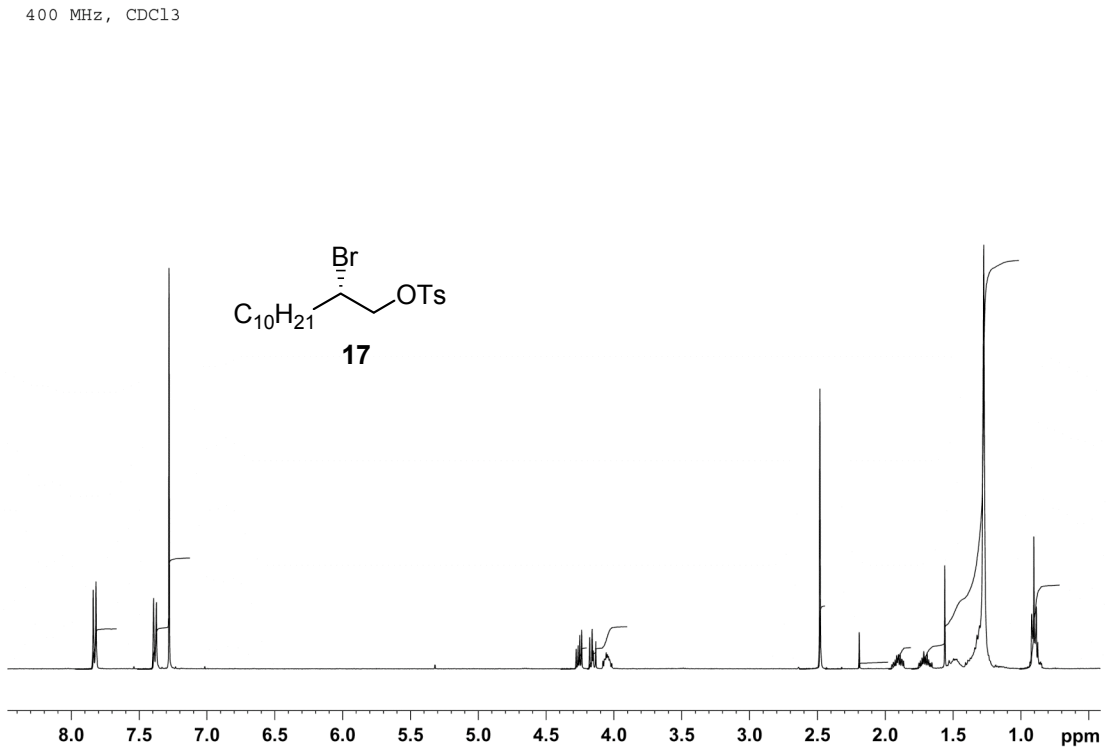
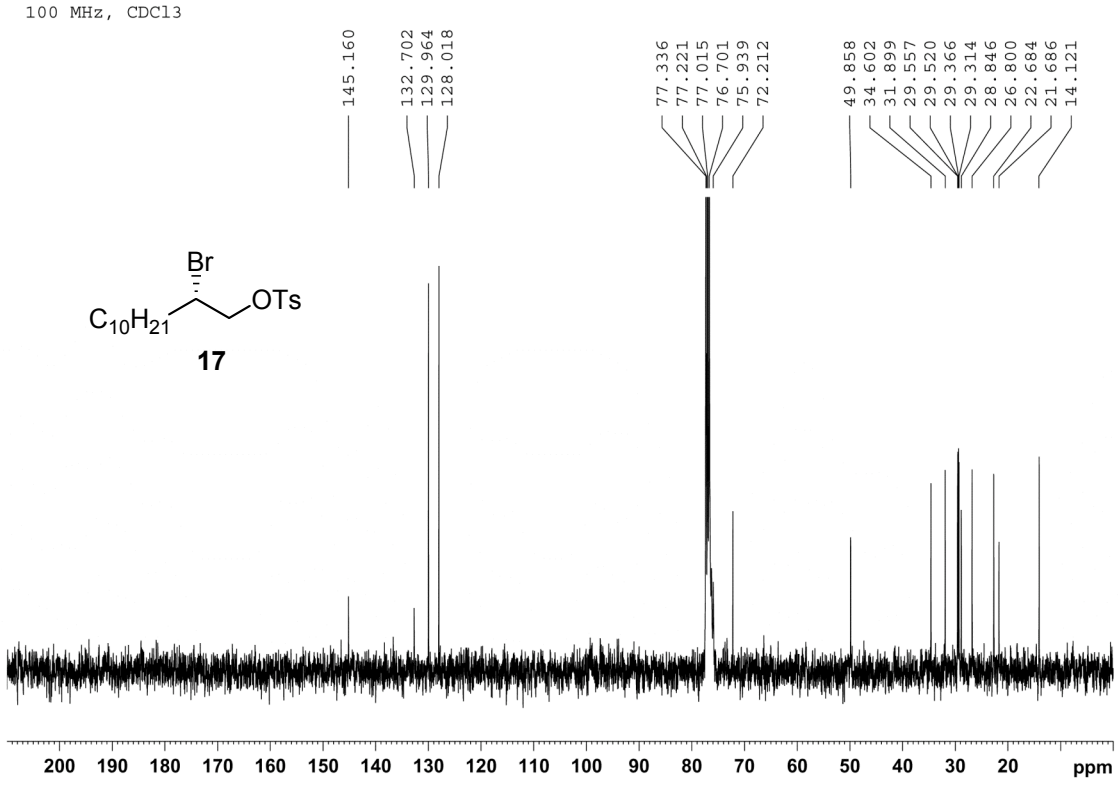
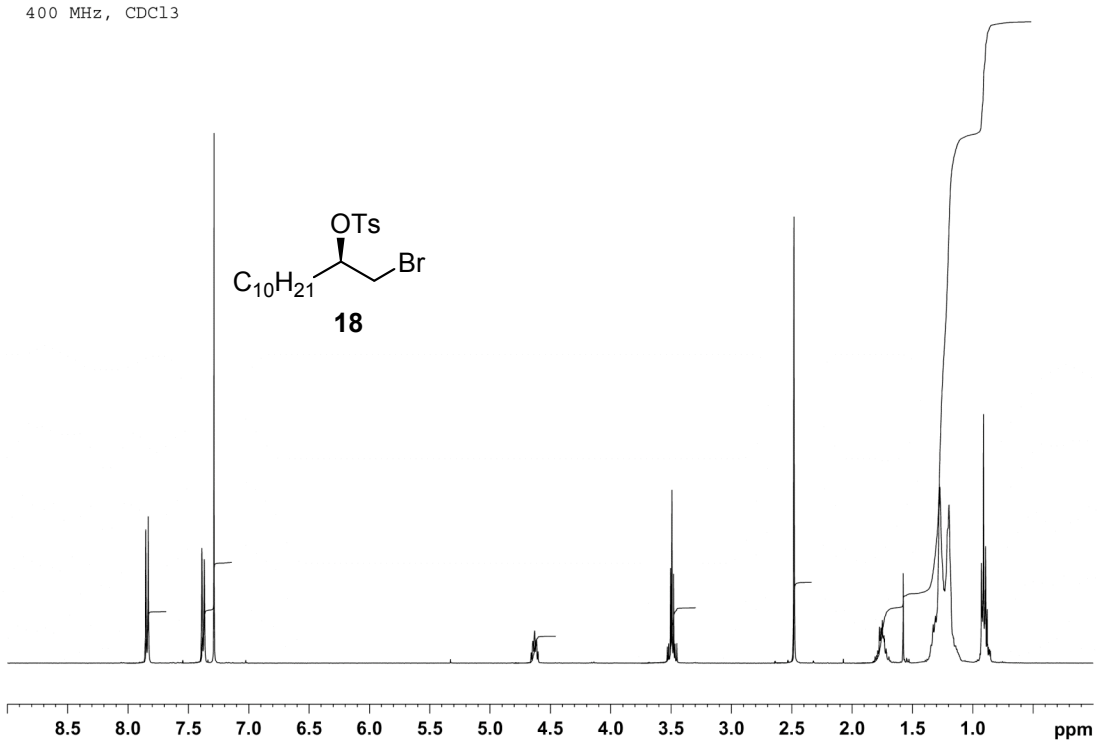


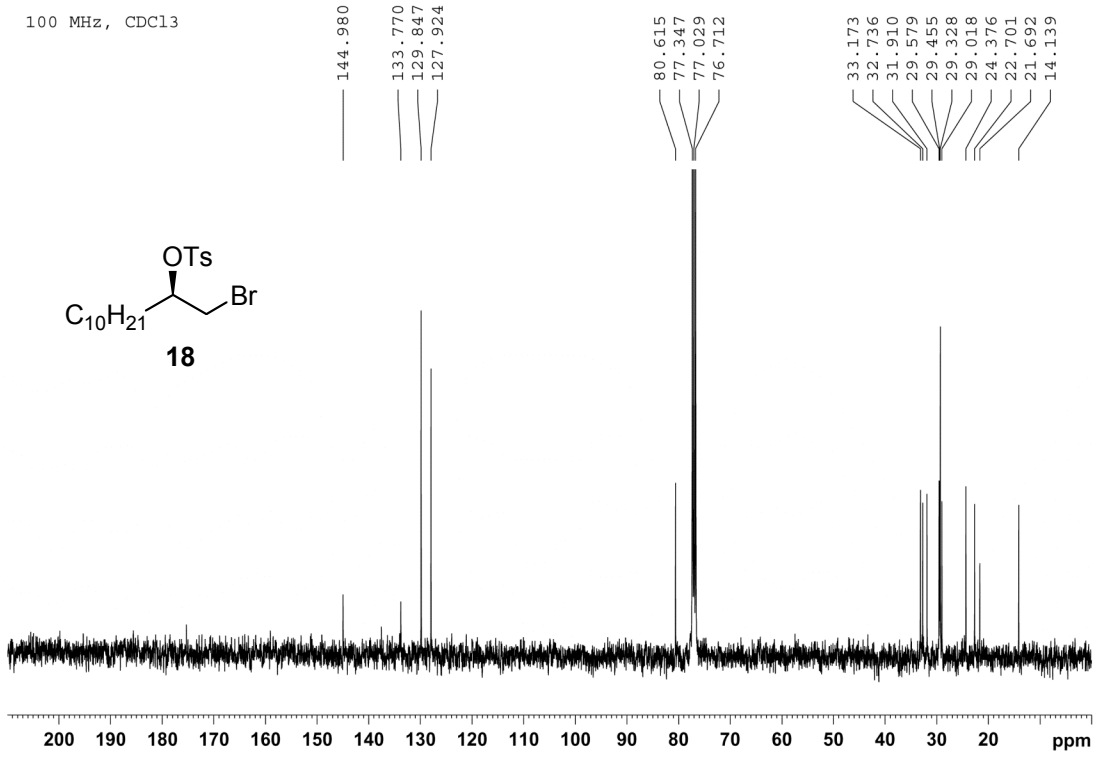
^{1}H NMR spectrum of tosylate **17**



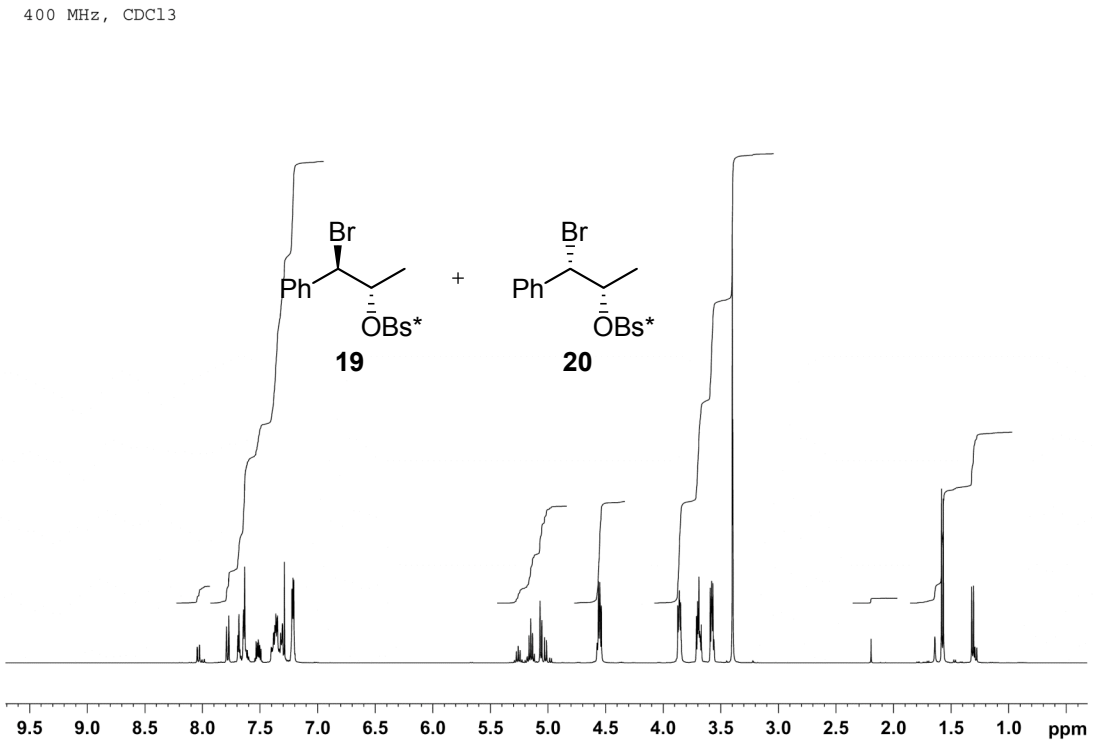
^{13}C NMR spectrum of tosylate **17**



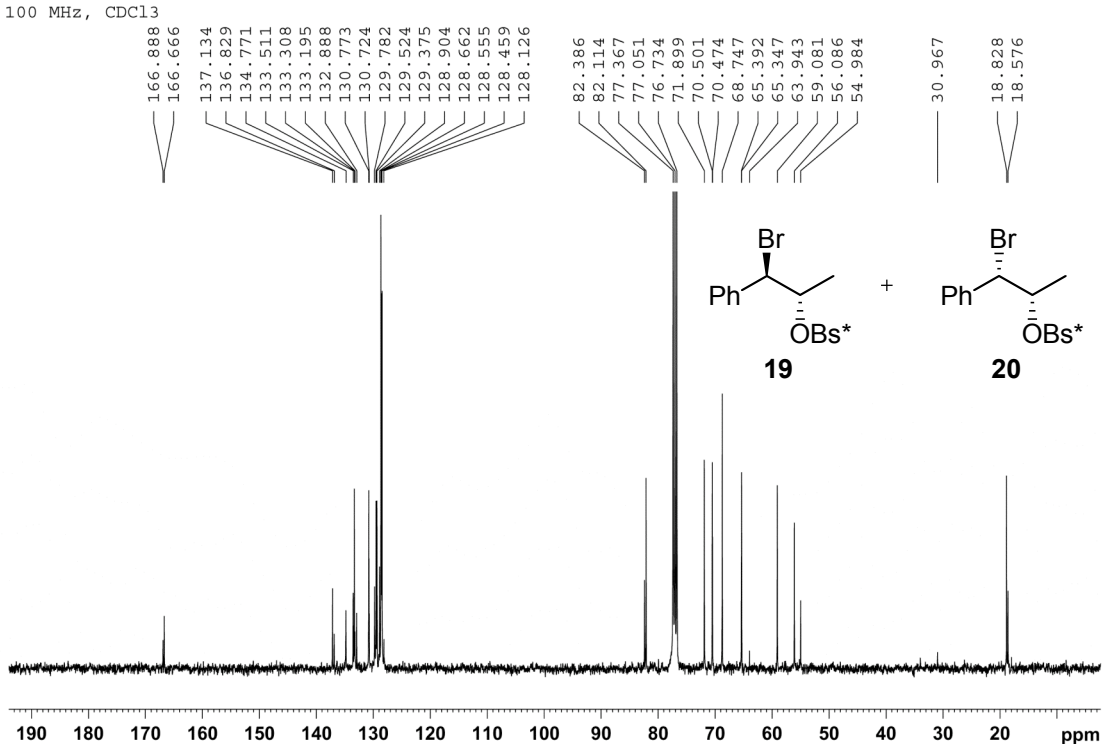
^{1}H NMR spectrum of tosylate **18**



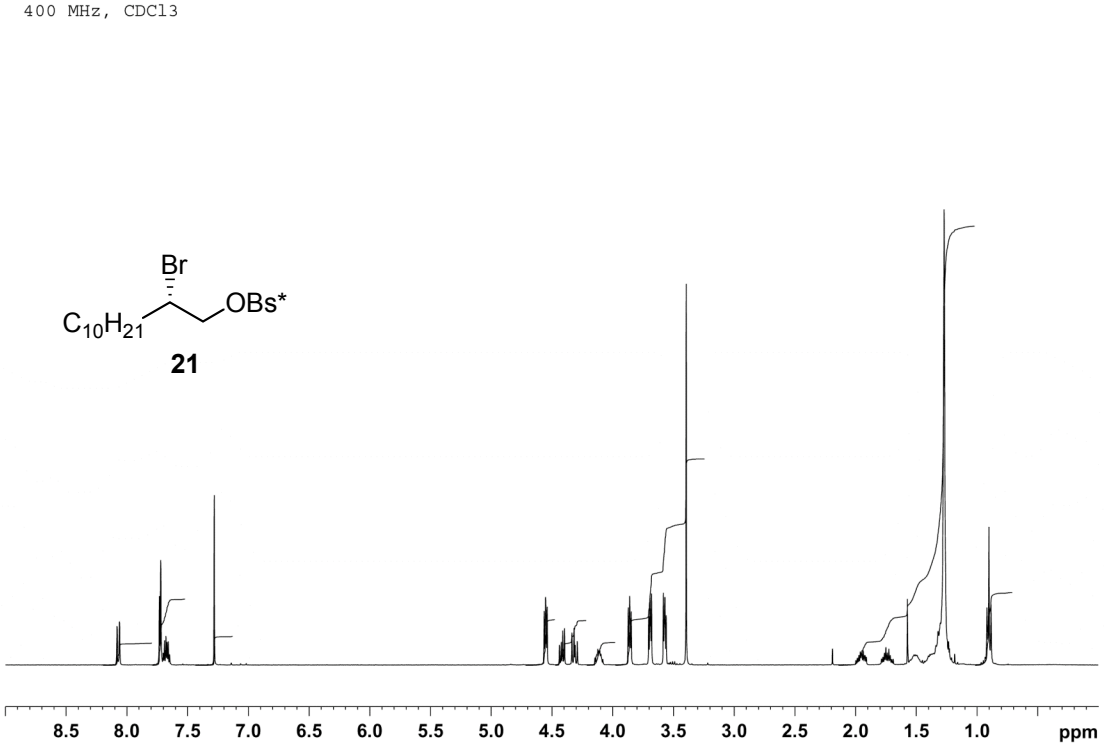
^{13}C NMR spectrum of tosylate **18**



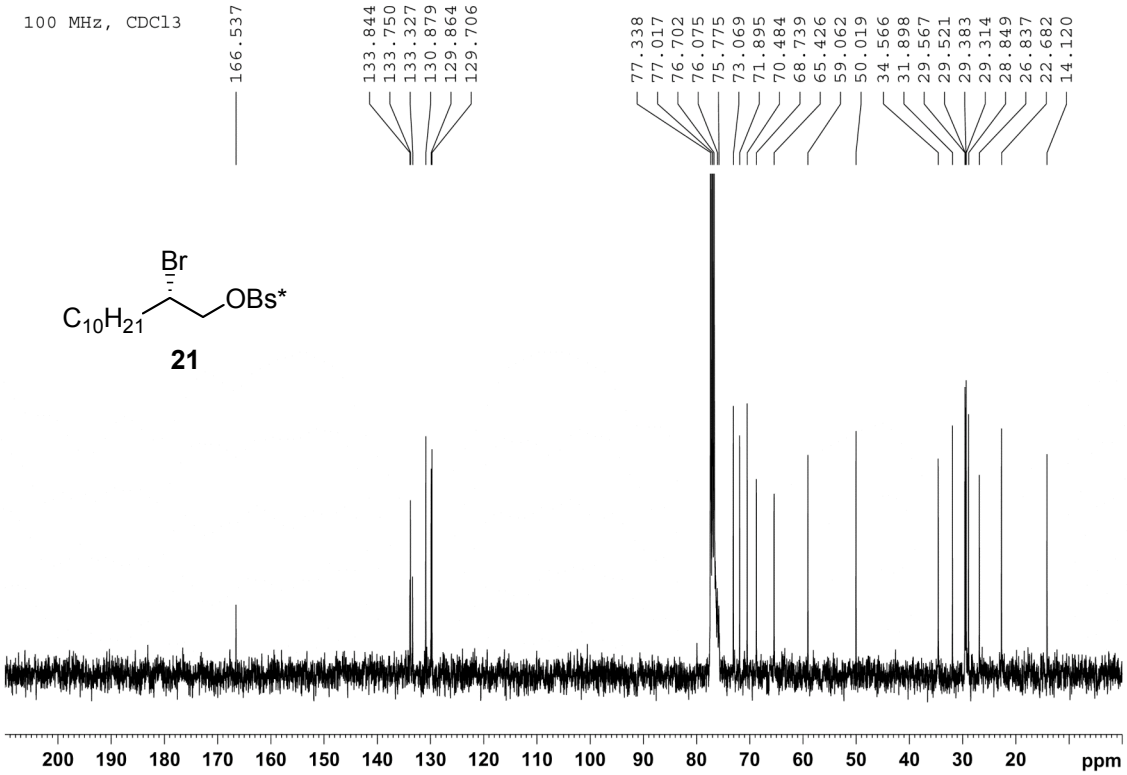
^{1}H NMR spectrum of benzenesulphonates **19** and **20**



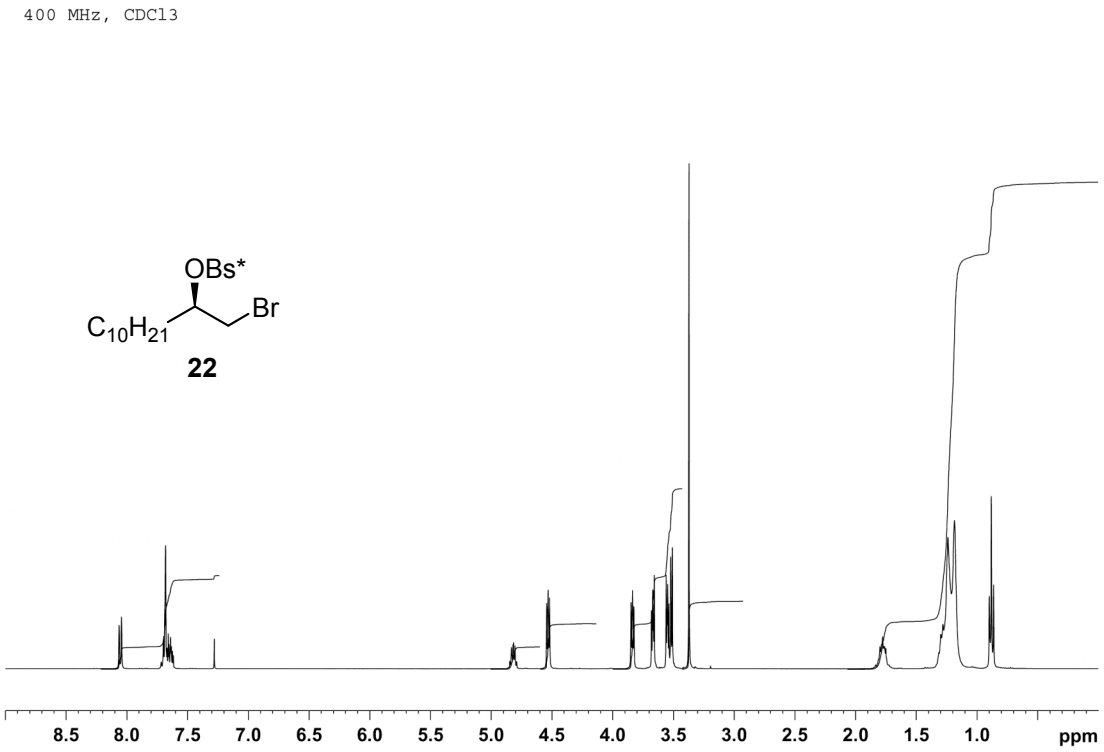
^{13}C NMR spectrum of benzenesulphonates **19** and **20**



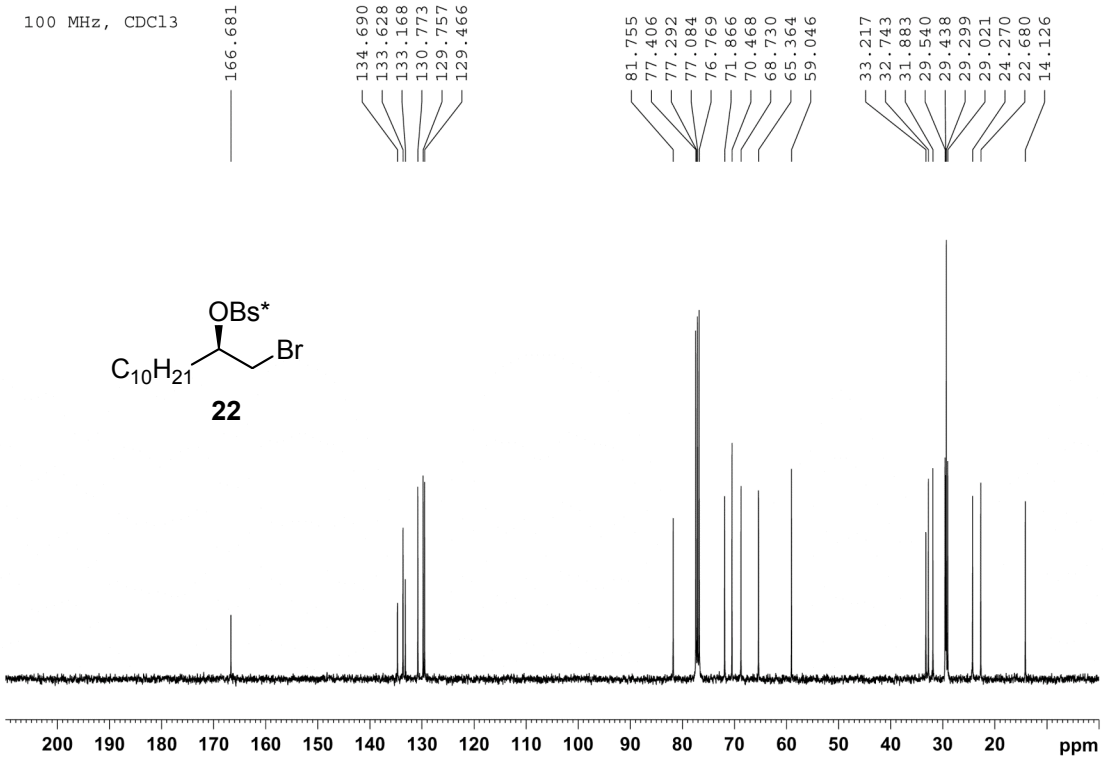
^{1}H NMR spectrum of benzenesulphonate **21**



^{13}C NMR spectrum of benzenesulphonate **21**



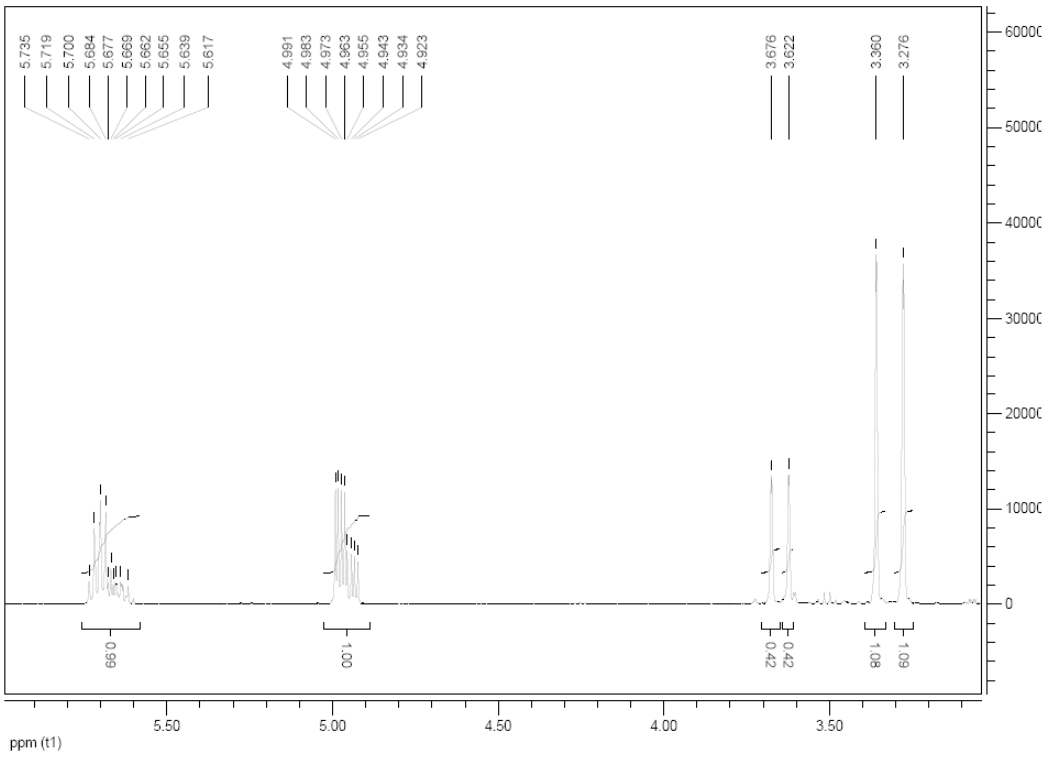
^{1}H NMR spectrum of benzenesulphonate **22**



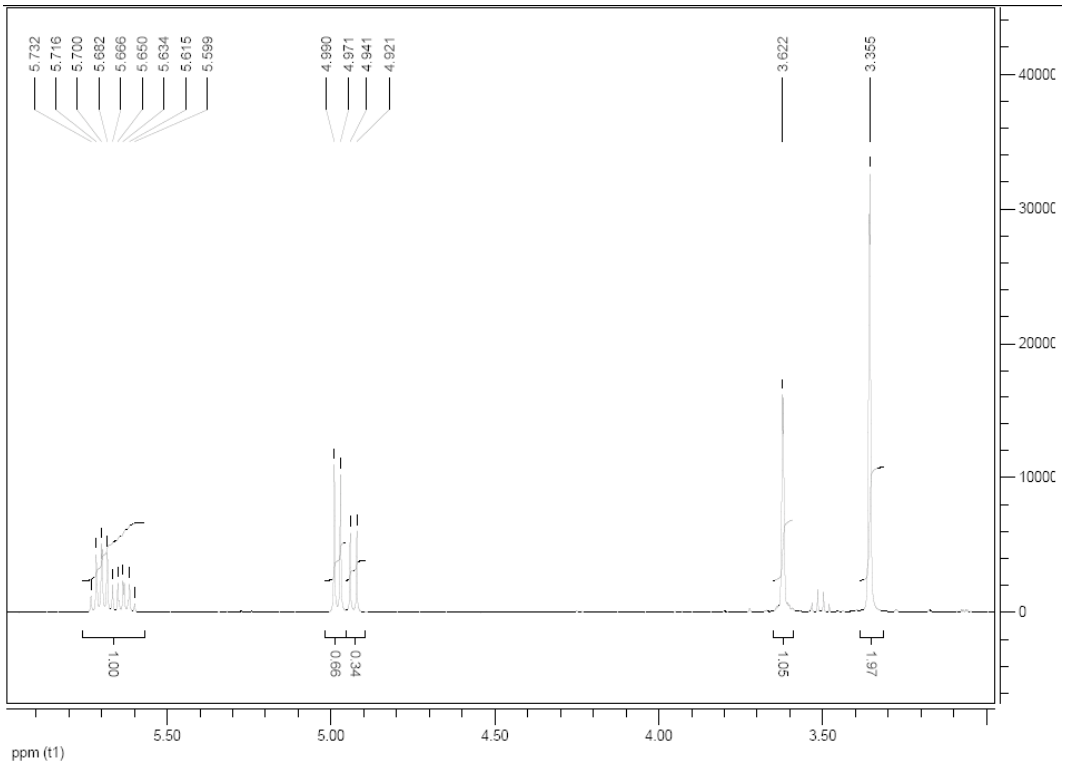
^{13}C NMR spectrum of benzenesulphonate **22**

Details of Mosher ester derivatives of **6**,**7**,**9**,**10**,**23** and **24**

Mosher ester analysis of 6 and 7. Racemic (1*R**,2*S**) and (1*S**,2*R**)-1-bromo-1-phenylpropan-2-ols (50 mg, 0.23 mmol) as a 73:23 mixture of diastereomers, triethylamine (81 μL, 0.58 mmol) and DMAP (57 mg, 0.46 mmol) were stirred in dichloromethane (2 mL) at RT under an inert atmosphere of nitrogen. (*S*)-Mosher acid chloride (117 mg, 0.46 mmol) was added as a 0.55M solution in deuterated chloroform and the reaction mixture was allowed to stir for 2.5 h. The reaction mixture was quenched with 0.1M aqueous hydrochloric acid (40 mL) and extracted with diethylether (40 mL). The organic layer was washed with a saturated aqueous solution of sodium hydrogen carbonate (40 mL), brine (40 mL), dried ($MgSO_4$), filtered and concentrated to give a colourless amorphous solid (99 mg, 98%), with ^{1}H NMR singlets in a 36:36:14:14 ratio at 3.28, 3.36, 3.61 and 3.68 ppm corresponding to the (1*S*,2*R*), (1*R*,2*S*), (1*S*,2*S*) and (1*R*,2*R*) *R*-Mosher ester derivatives respectively. An identical analysis using enantiopure **6** and **7** in a 68:32 ratio gave only the singlets in the ^{1}H NMR at 3.36 and 3.61 ppm in a 65:35 ratio respectively. The ^{1}H NMR spectra follow.

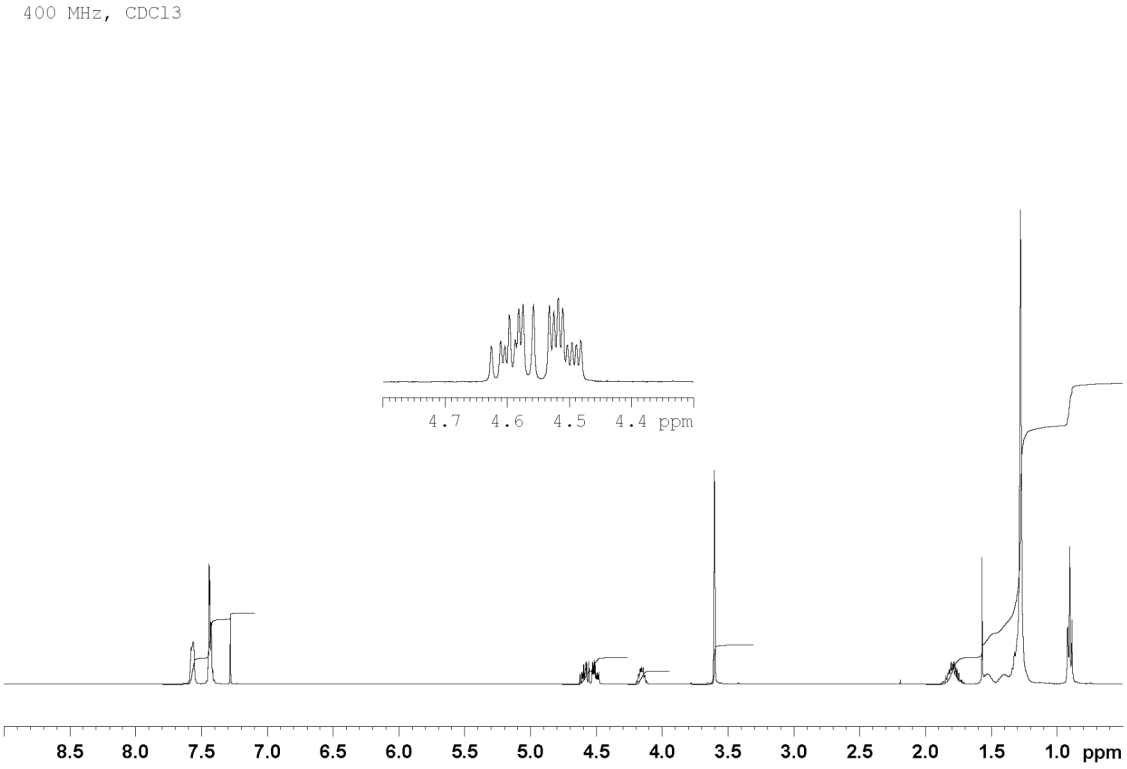


^{1}H NMR spectrum of Mosher's esters of (±)-**6** and (±)-**7**

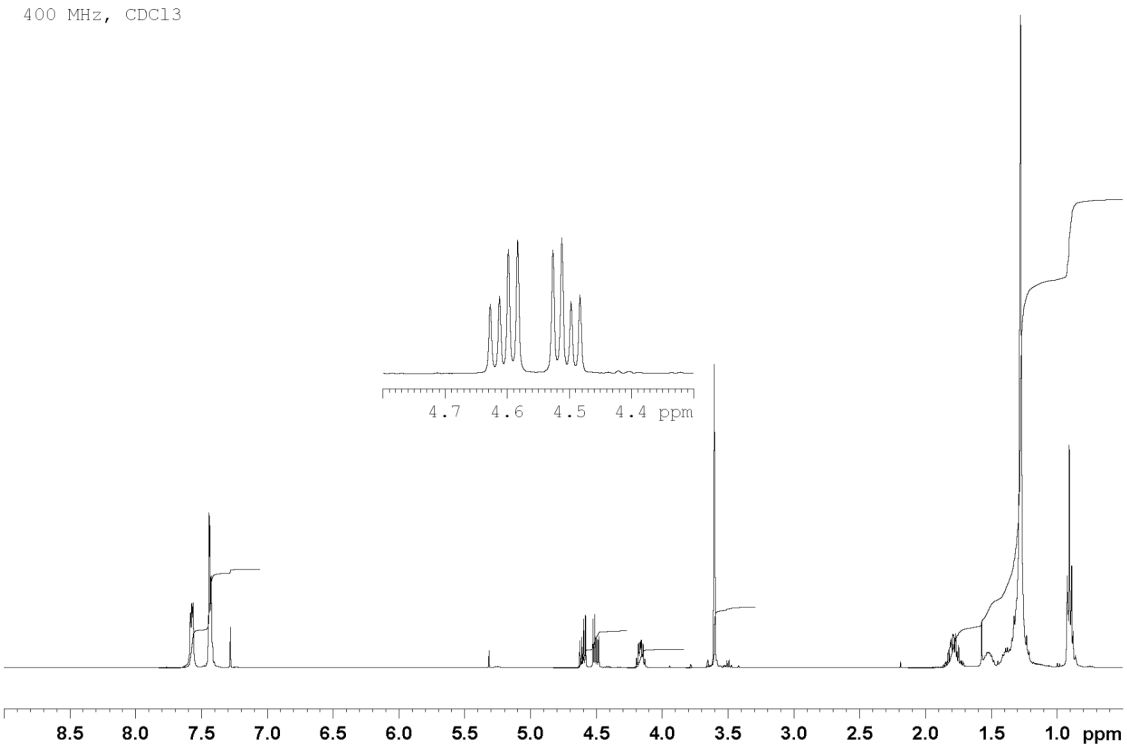


^{1}H NMR spectrum of Mosher's esters of (1*R*,2*S*)-**6** and (1*S*,2*S*)-**7**

Mosher's ester anaylsis of 9. To a stirred solution of racemic **9** (20 mg, 0.08 mmol) in dichloromethane (0.5 mL) was added triethylamine (32 μL, 0.23 mmol) and DMAP (19 mg, 0.15 mmol), followed by a solution of (*S*)-Mosher acid chloride (38 mg, 0.15 mmol) in dichloromethane (0.8 mL). After stirring for 30 min, the reaction was quenched by the addition of 0.1M HCl solution (5 mL), and diluted with dichloromethane (10 mL). The separated organic phase was washed with saturated sodium carbonate solution (5 mL) and dried over magnesium sulfate. The solvent was removed *in vacuo* to give the title compound (36 mg, >99% yield) as a colourless oil. An identical analysis was performed on (*S*)-**9** showing it to be enantiomerically pure. The ^{1}H NMR spectra follow:

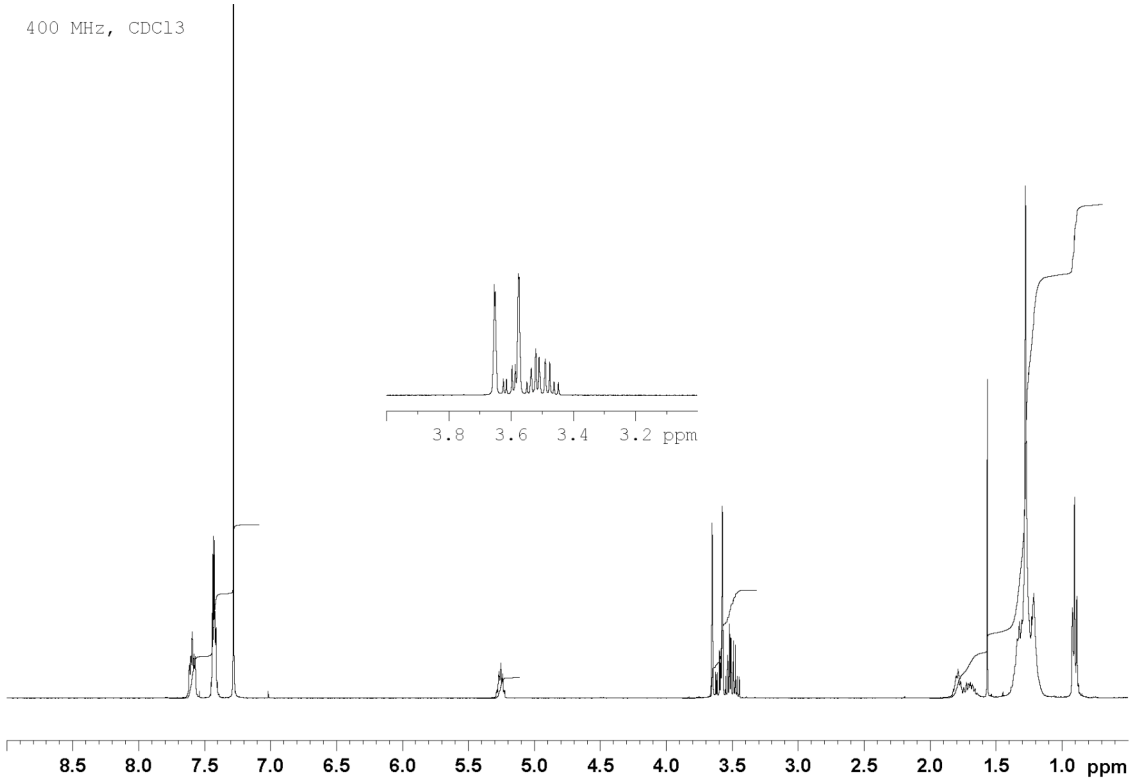


^{1}H NMR spectrum of Mosher's ester of (±)-**9**

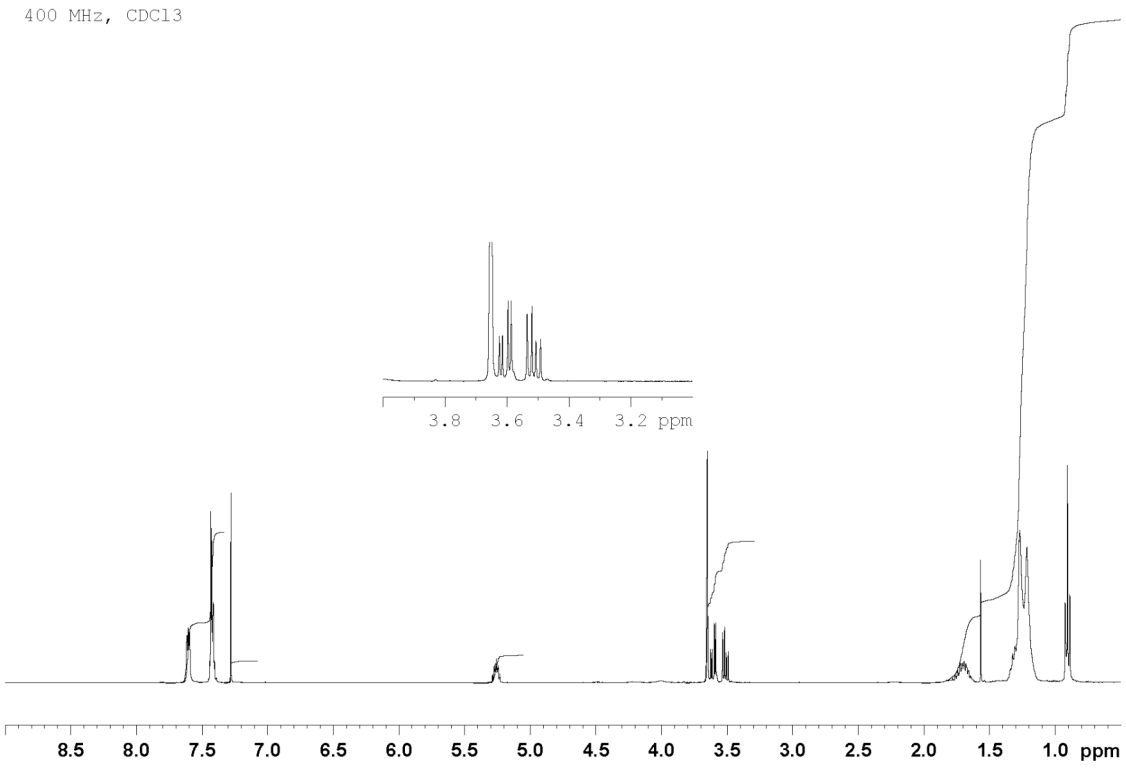


^{1}H NMR spectrum of Mosher's ester of *(S)*-**9**

Mosher's ester anaylsis of 10. To a stirred solution of racemic **10** (20 mg, 0.08 mmol) in dichloromethane (0.5 mL) was added triethylamine (32 μL, 0.23 mmol) and DMAP (19 mg, 0.15 mmol), followed by a solution of (*S*)-Mosher acid chloride (38 mg, 0.15 mmol) in dichloromethane (0.8 mL). After stirring for 30 min, the reaction was quenched by the addition of 0.1M HCl solution (5 mL), and diluted with dichloromethane (10 mL). The separated organic phase was washed with saturated sodium carbonate solution (5 mL) and dried over magnesium sulfate. The solvent was removed *in vacuo* to give the title compound (36 mg, >99% yield) as a colourless oil. An identical analysis was performed on (*R*)-**10** showing it to be enantiomerically pure. The ^{1}H NMR spectra follows:

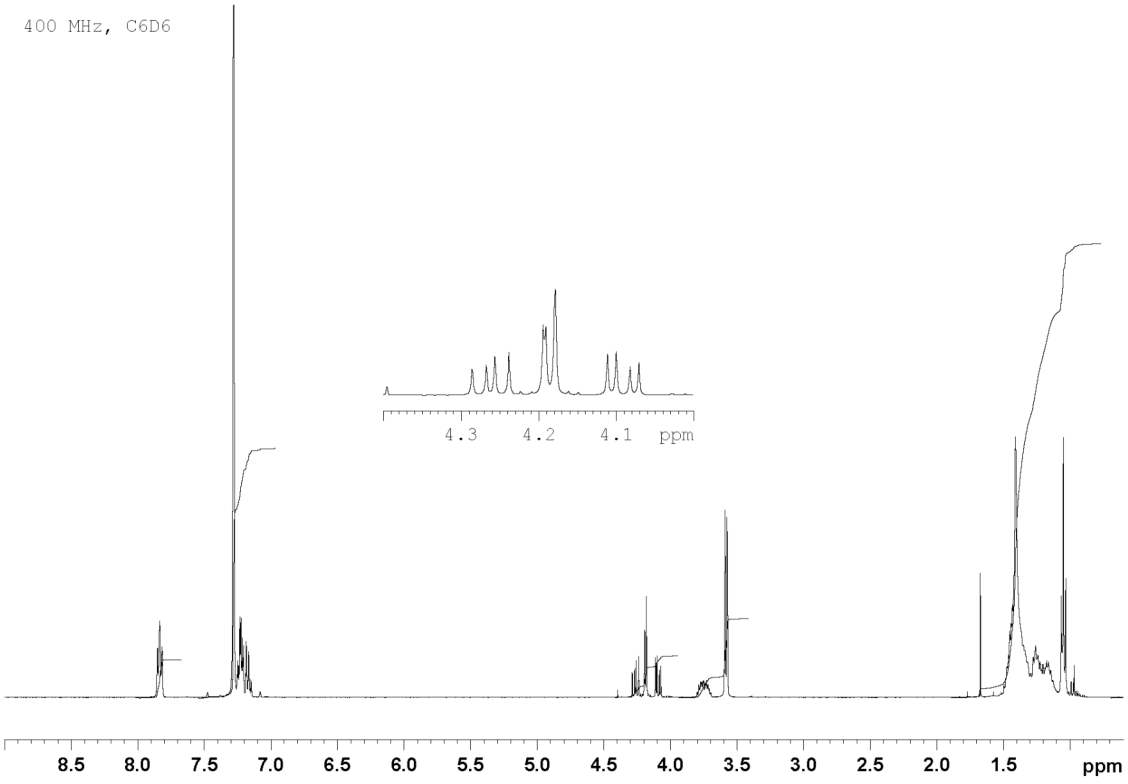


^{1}H NMR spectrum of Mosher's ester of (±)-**10**

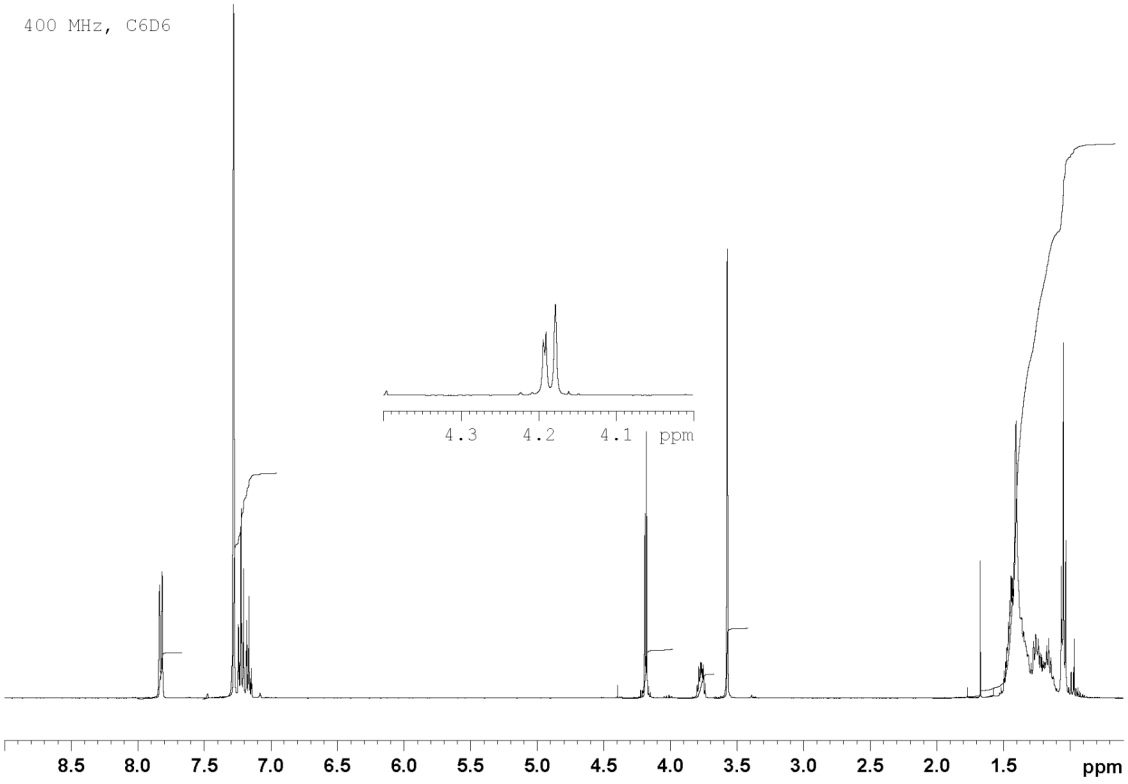


^{1}H NMR spectrum of Mosher's ester of (*R*)-**10**

Mosher's ester anaylsis of 23. To a stirred solution of racemic **23** (17 mg, 0.08 mmol) in dichloromethane (0.5 mL) was added triethylamine (32 μL, 0.23 mmol) and DMAP (19 mg, 0.15 mmol), followed by a solution of (*S*)-Mosher acid chloride (38 mg, 0.15 mmol) in dichloromethane (0.8 mL). After stirring for 30 min, the reaction was quenched by the addition of 0.1M HCl solution (5 mL), and diluted with dichloromethane (10 mL). The separated organic phase was washed with saturated sodium carbonate solution (5 mL) and dried over magnesium sulfate. The solvent was removed *in vacuo* to give the title compound (34 mg, >99% yield) as a colourless oil. An identical analysis was performed on (*S*)-**23** showing it to be enantiomerically pure. The ^{1}H NMR spectra follow:

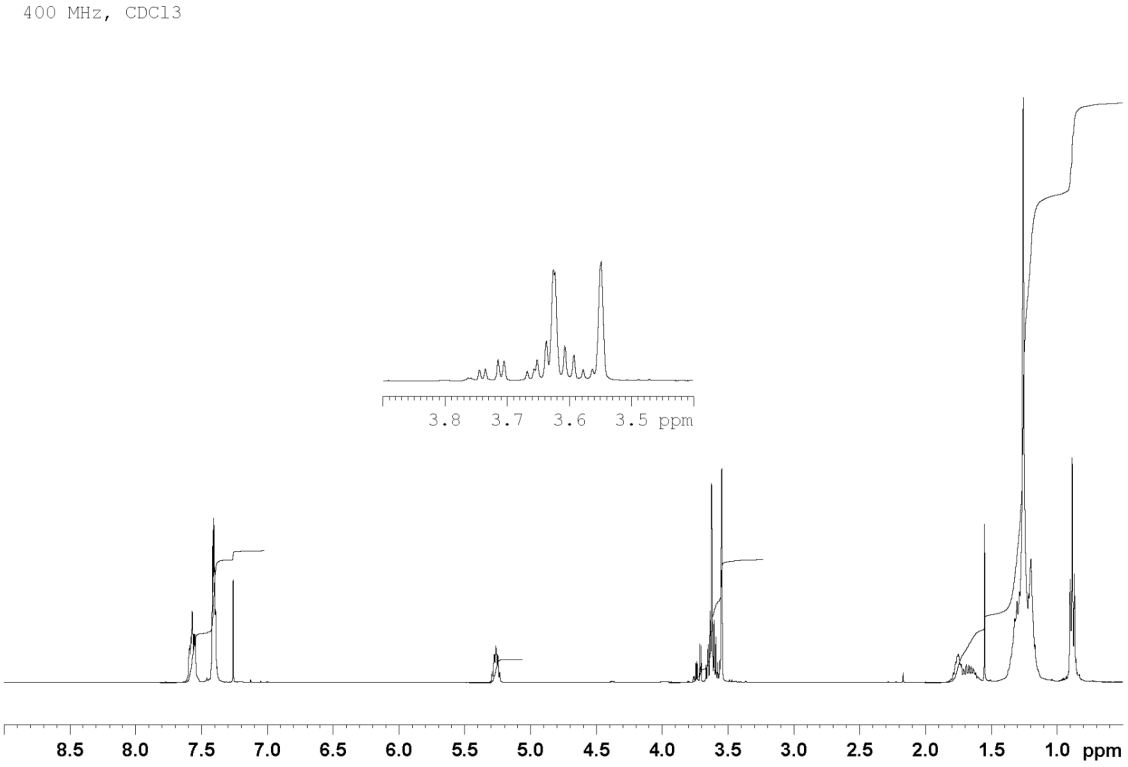


^{1}H NMR spectrum of Mosher's ester of (±)-**23**

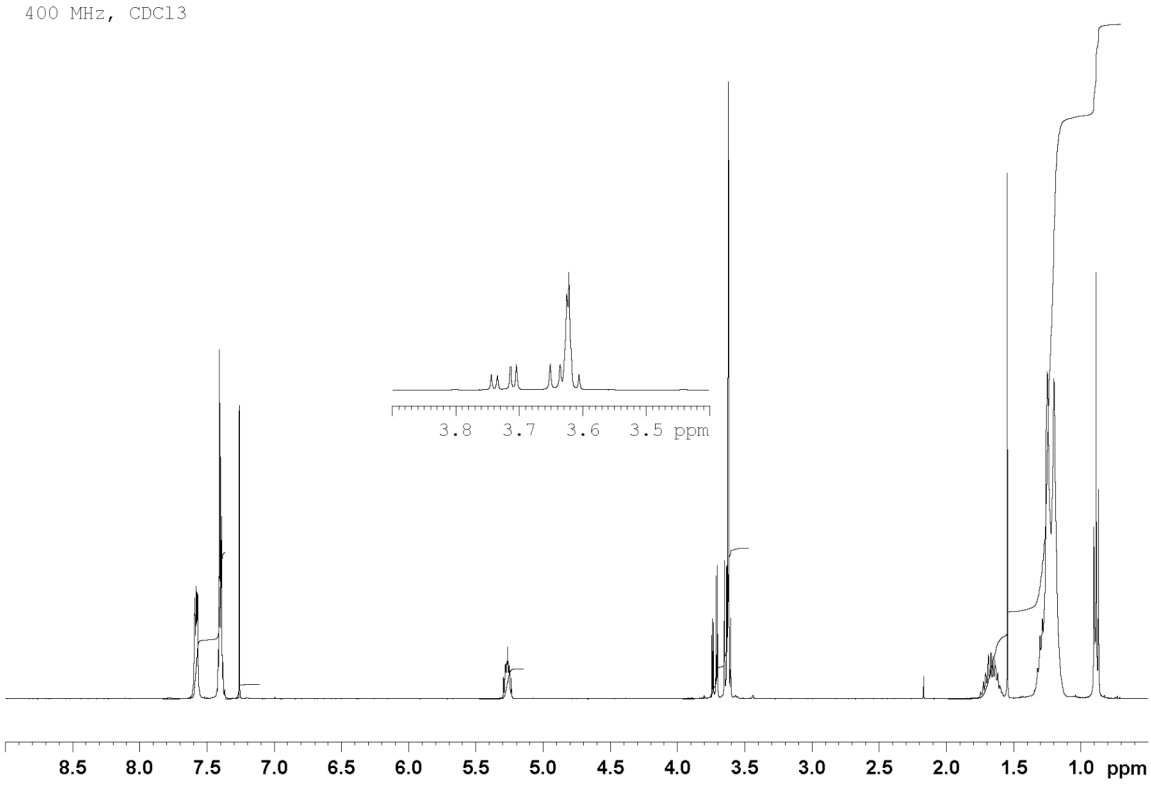


^{1}H NMR spectrum of Mosher's ester of (*S*)-**23**

Mosher's ester anaylsis of 24. To a stirred solution of racemic **24** (17 mg, 0.08 mmol) in dichloromethane (0.5 mL) was added triethylamine (32 μL, 0.23 mmol) and DMAP (19 mg, 0.15 mmol), followed by a solution of (*S*)-Mosher acid chloride (38 mg, 0.15 mmol) in dichloromethane (0.8 mL). After stirring for 30 min, the reaction was quenched by the addition of 0.1M HCl solution (5 mL), and diluted with dichloromethane (10 mL). The separated organic phase was washed with saturated sodium carbonate solution (5 mL) and dried over magnesium sulfate. The solvent was removed *in vacuo* to give the title compound (34 mg, >99% yield) as a colourless oil. An identical analysis was performed on (*R*)-**24** showing it to be enantiomerically pure. The ^{1}H NMR spectra follow:

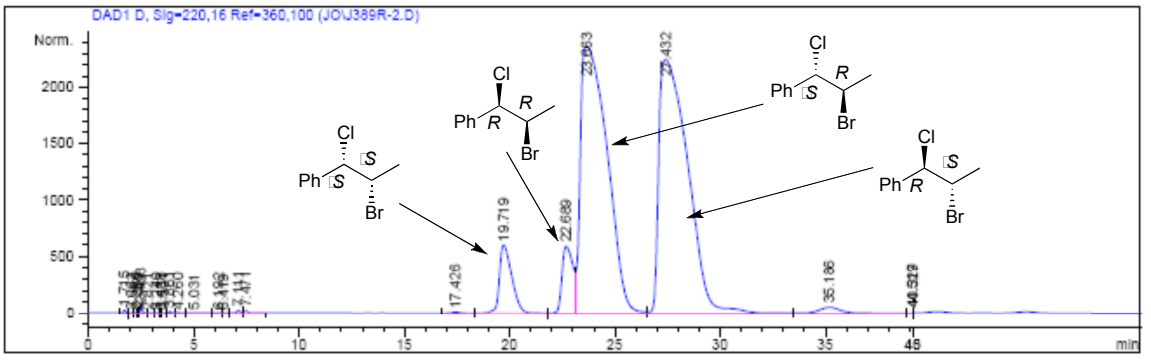


^{1}H NMR spectrum of Mosher's ester of (±)-**24**

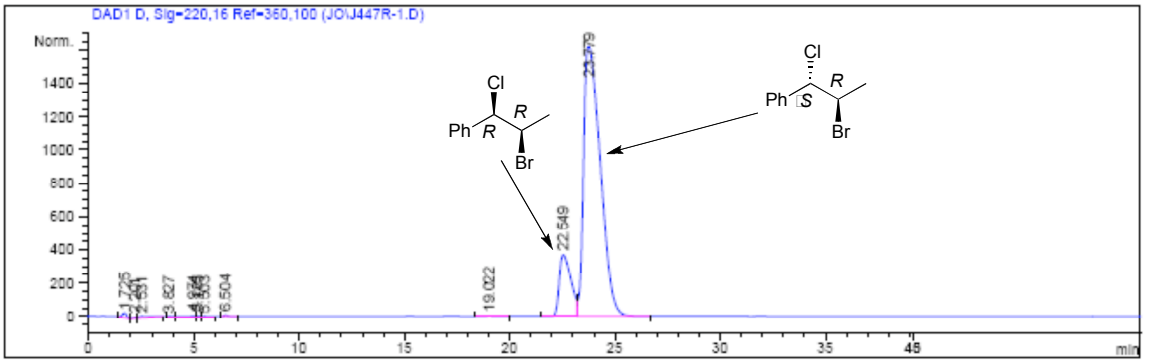


^{1}H NMR spectrum of Mosher's ester of (*R*)-**24**

Chiral HPLC analysis of **11&12**



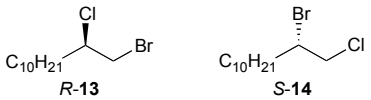
Chiral HPLC trace demonstrating separation of diastereomeric (1*S**,2*R**) and (1*R**,2*R**)-2-bromo-1-chloro-1-phenylpropane **11** and **12** into their enantiomers.



Chiral HPLC trace showing formation of enantiomerically pure (1*S*,2*R*) and (1*R*,2*R*)-2-bromo-1-chloro-1-phenylpropanes **11** and **12** from the prototypical reaction of benzenesulphonate mixture **19&20** with $TiCl_4$.

Optical rotation measurements, NMR integration and ee calculations for **13** and **14**

The enantiomeric purity of the bromohydrin mixture was assessed by a two-step procedure. ^{1}H NMR integration of two regioisomers of **13** and **14** gave their ratio (see figures below). A comparison of the measured optical rotation compared to the calculated rotation of the mixture based on the known rotations of individually prepared enantiopure *S*-**13** ($[\alpha]_D$ -29) and *S*-**14** ($[\alpha]_D$ -32) gave the enantiomeric purity.



R-**13** $[\alpha]_D$ = +29.0 *S*-**14** $[\alpha]_D$ = -32.0

Table Entry[a]	% yield[b]	% **13**[c]	% **14**[c]	measured rotation[d]	Calculated rotation[e]	% ee[f]
4	57	58	42	+2.6	3.38	77±5
5	53	58	42	+2.3	3.38	68±5
6	95	87	13	+21.0	21.07	100±5
7	87	86	14	+21.0	20.46	103±5
8	92	76	24	+15.0	14.36	104±5
9	>95	71	29	+11.7	11.31	103±5

a Table entry in main manuscript;

b After column chromatography;

c As determined by integration of the relevant portion of the ^{1}H NMR spectrum;

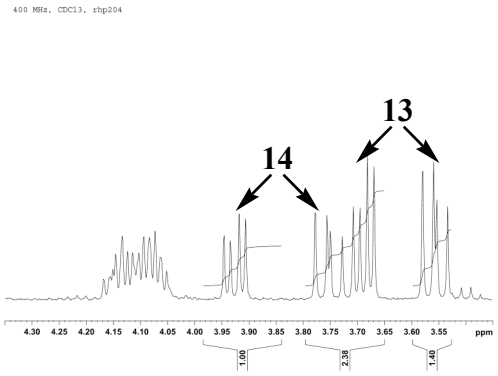
d Optical rotations recorded at *c* = 0.3, CH_2Cl_2, 24˚C;

e Calculated as [optical rotation of mixture/(0.01*((%**13** *29)+(%**14***-32)))] at 100% ee;

f Calculated as measured rotation/calculated rotation. The error is estimated to be ±5%.

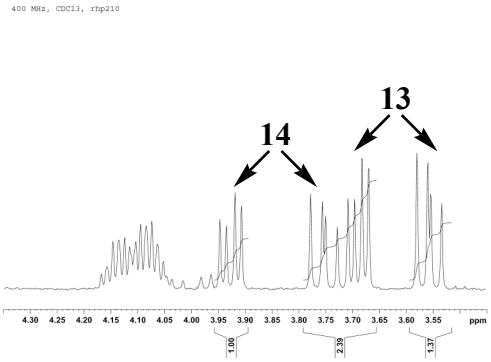
^{1}H NMR spectra for entries in Table 1

Entry 4



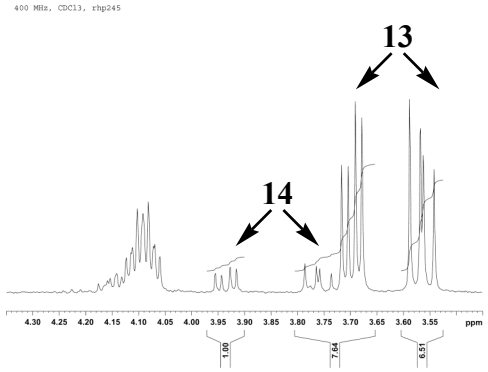
Ratio of **13:14** = 58:42

Entry 5



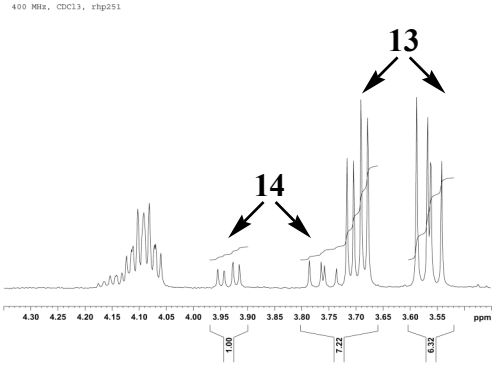
Ratio of **13:14** = 58:42

Entry 6



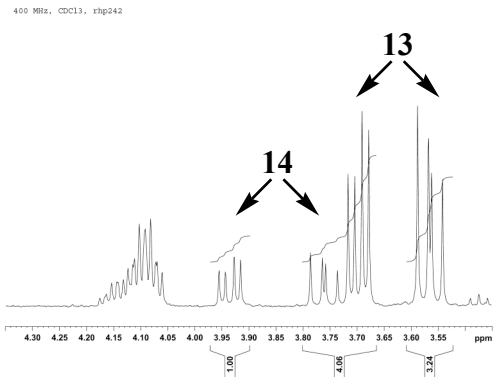
Ratio of **13:14** = 87:13

Entry 7



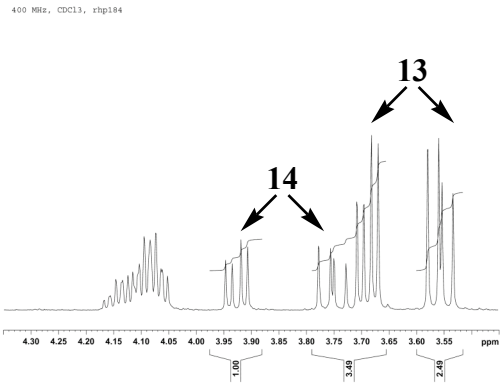
Ratio of **13:14** = 86:14

Entry 8



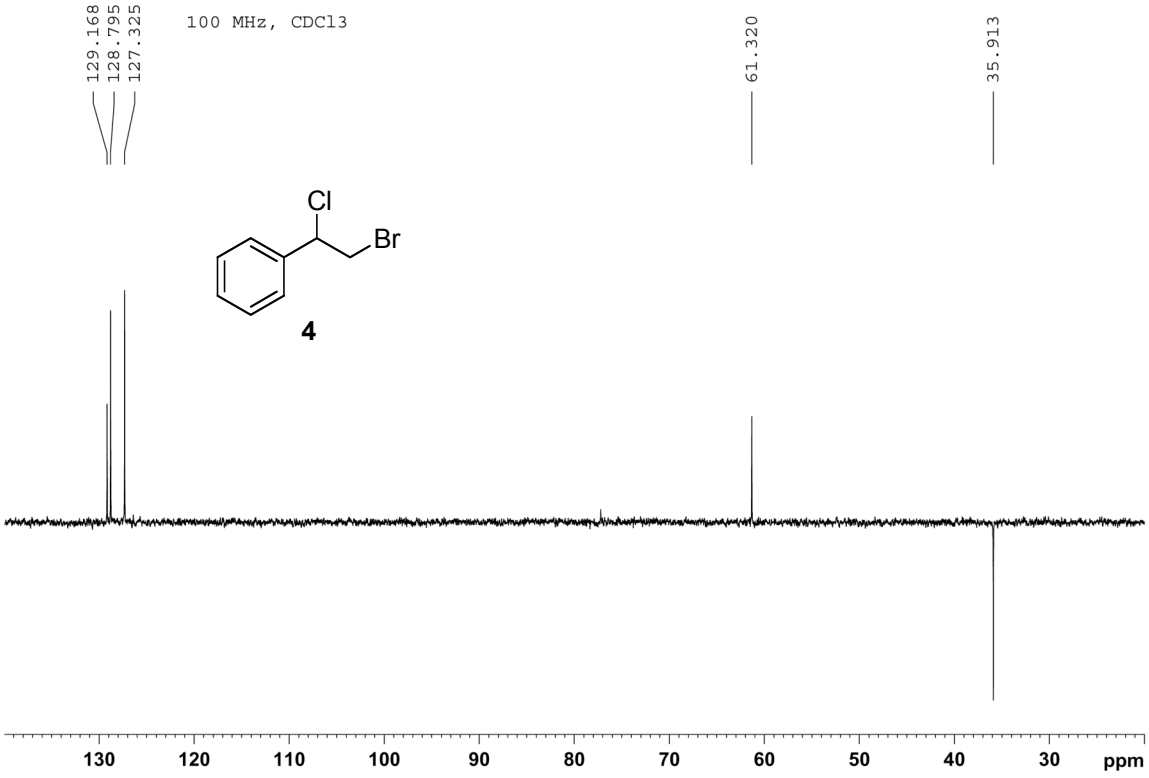
Ratio of **13:14** = 76:24

Entry 9

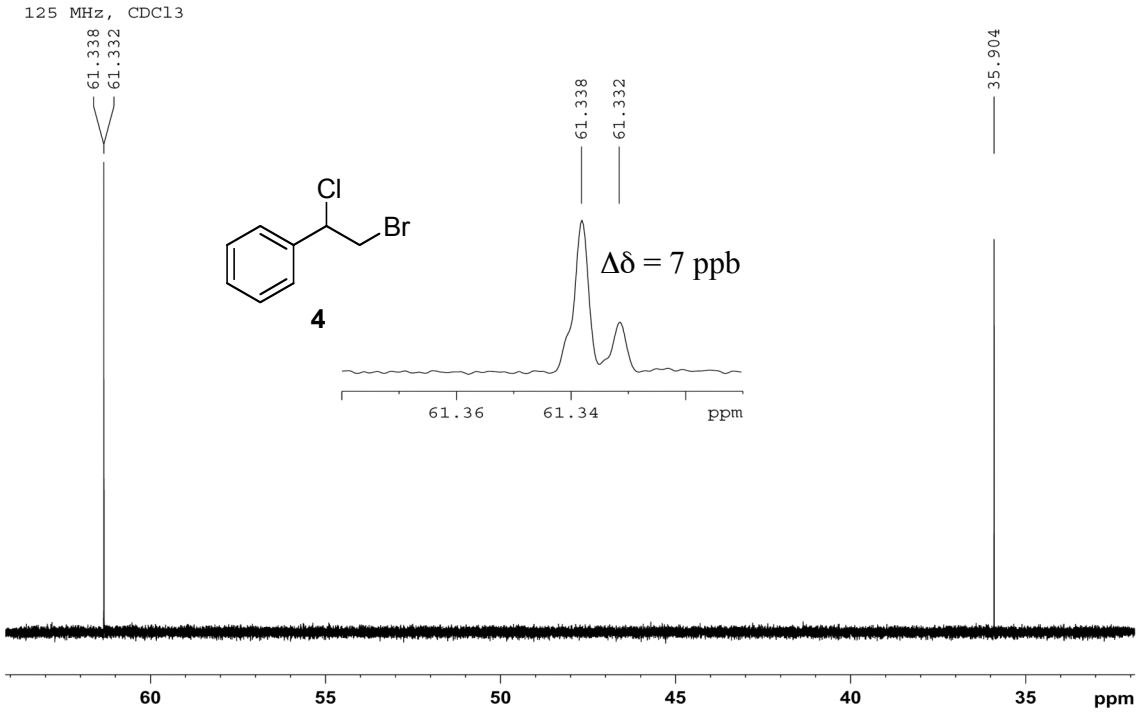


Ratio of **13:14** = 71:29

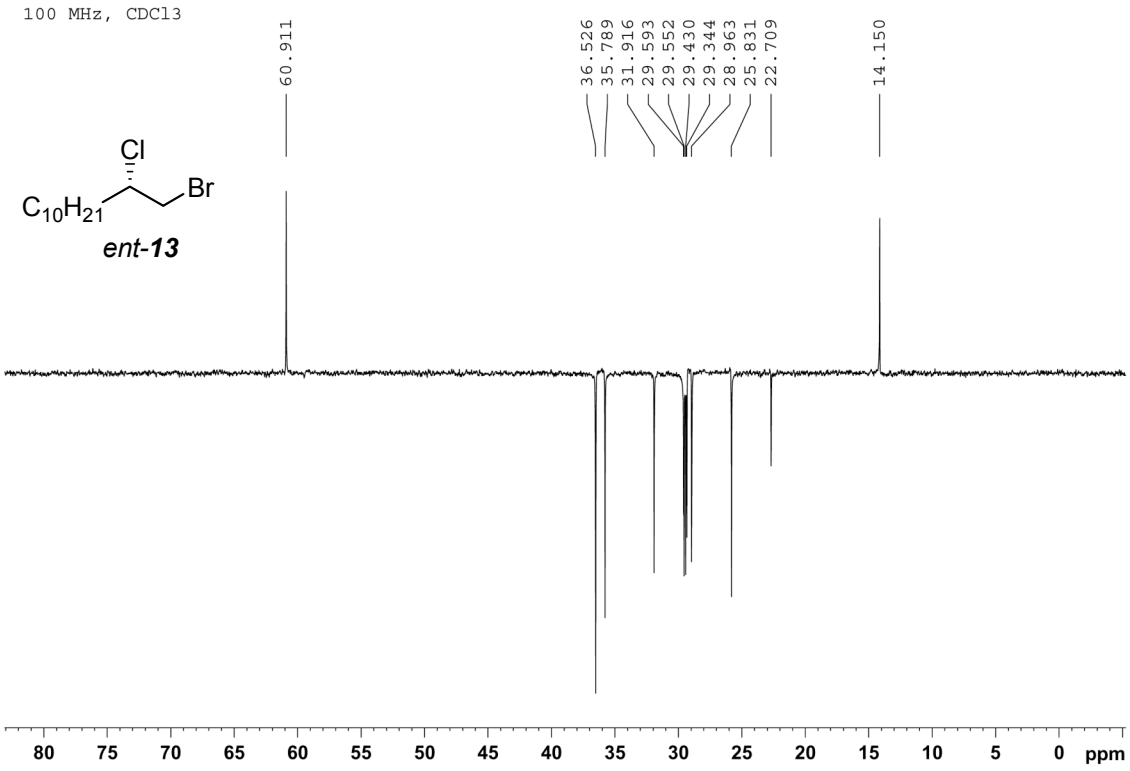
Copies of ^{13}C NMR spectra showing halide-induced isotopic shifts for **4**, **13**, **14**, **23** and **24**



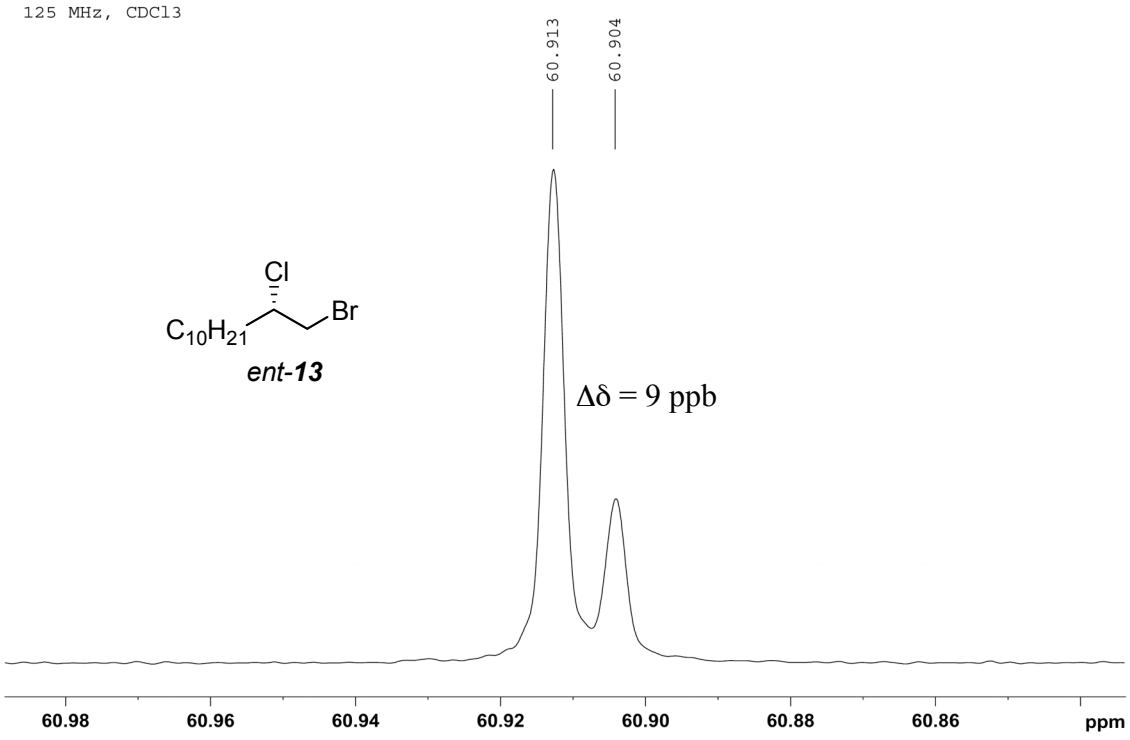
DEPT 135 spectrum of bromochloride **4** (CH_2 negative)



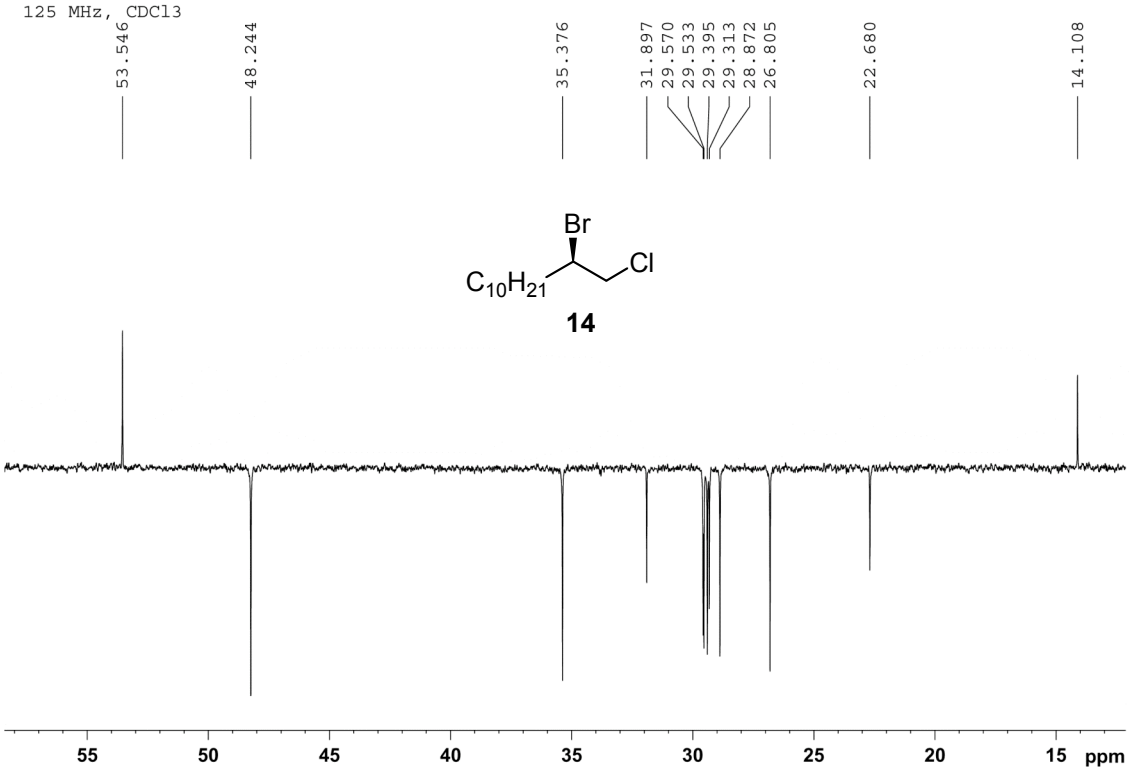
^{13}C NMR of bromochloride **4** showing chlorine-induced isotopic shift



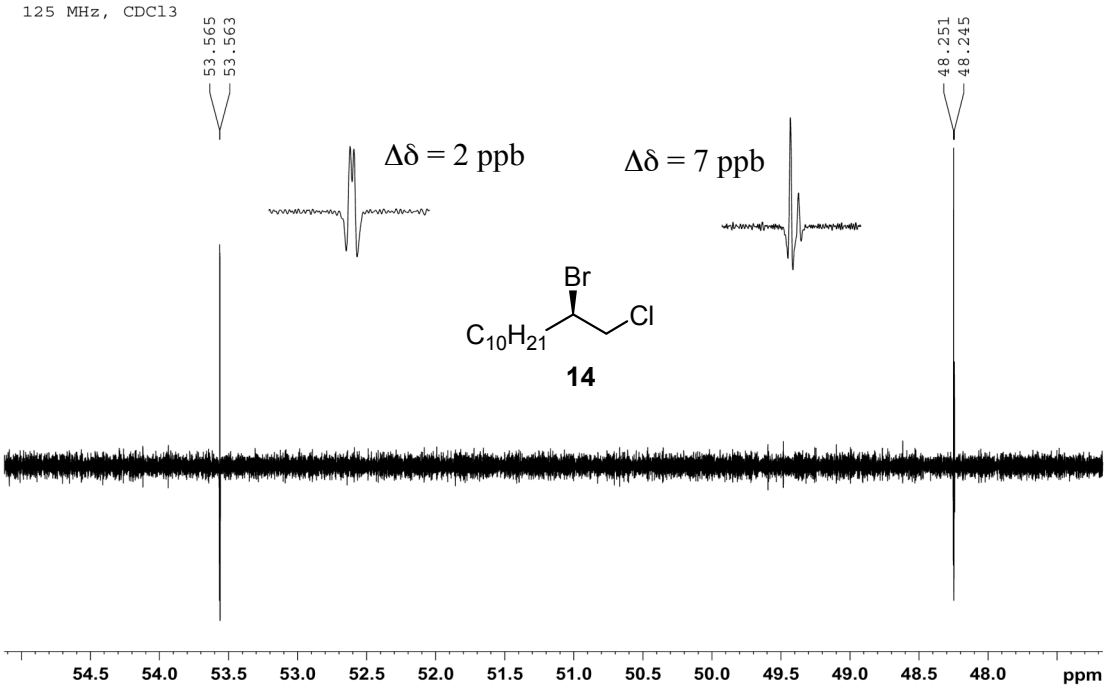
DEPT 135 spectrum of bromochloride **13** (CH_2 negative)



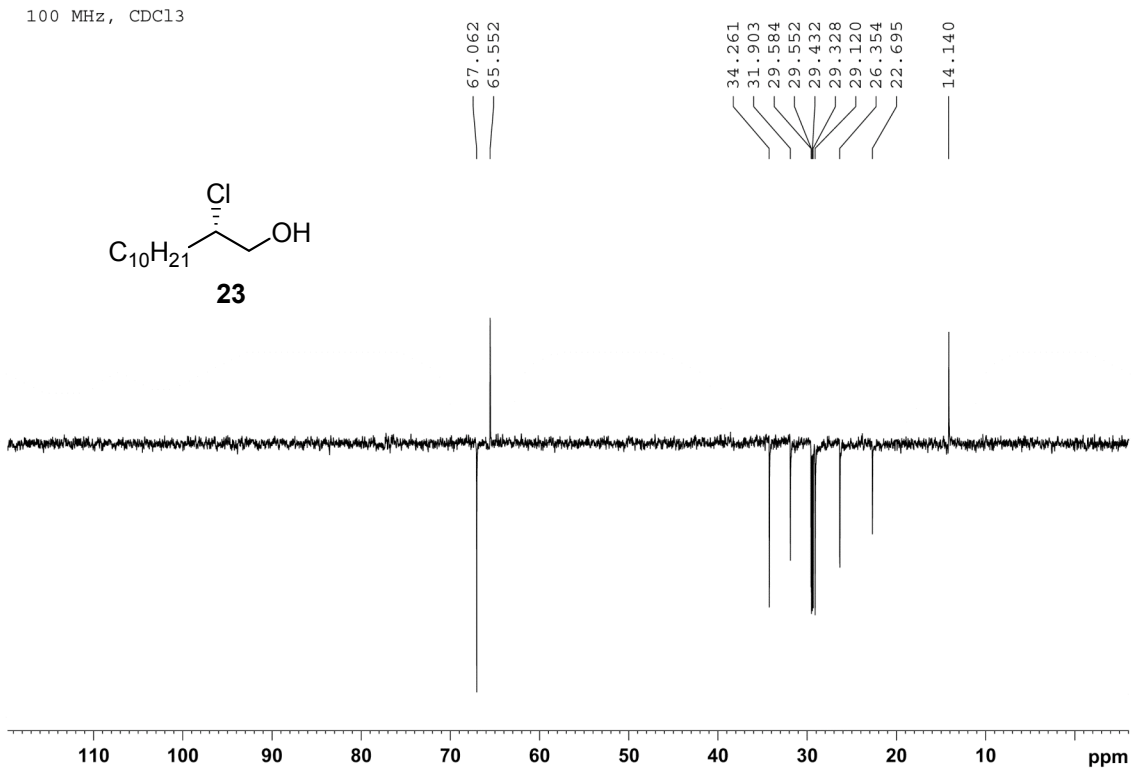
^{13}C NMR of bromochloride **13** showing chlorine-induced isotopic shift



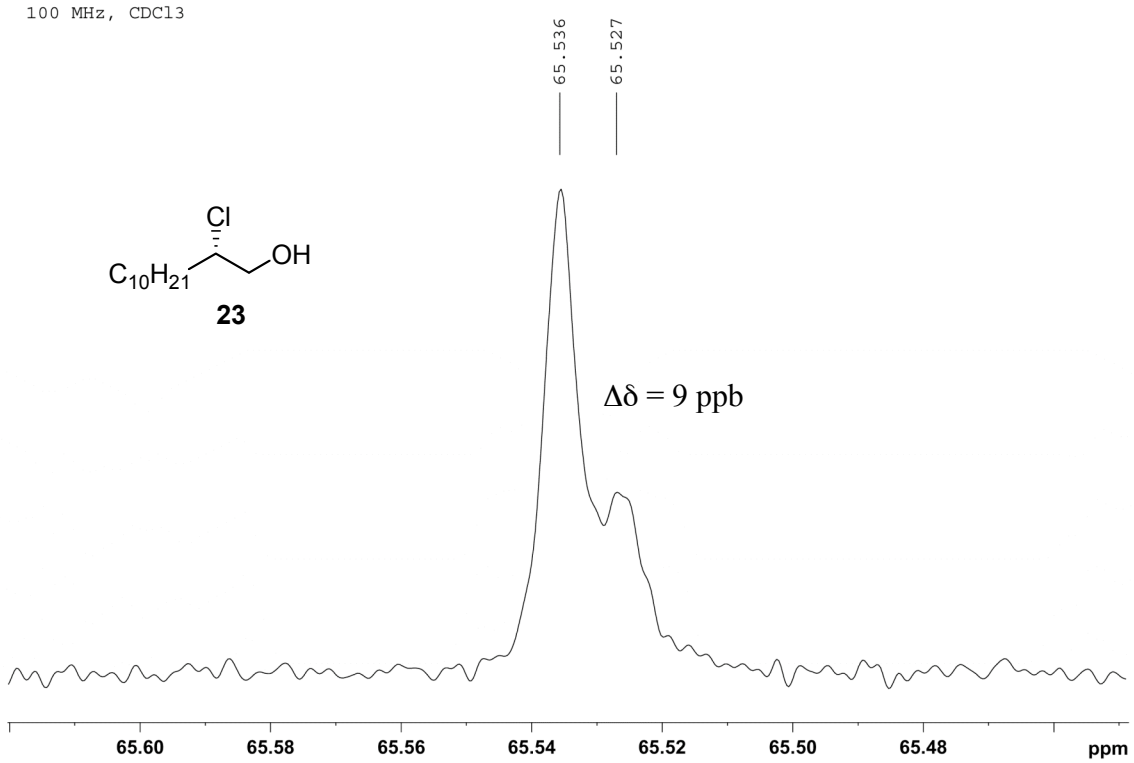
DEPT 135 spectrum of bromochloride **14** (CH_2 negative)



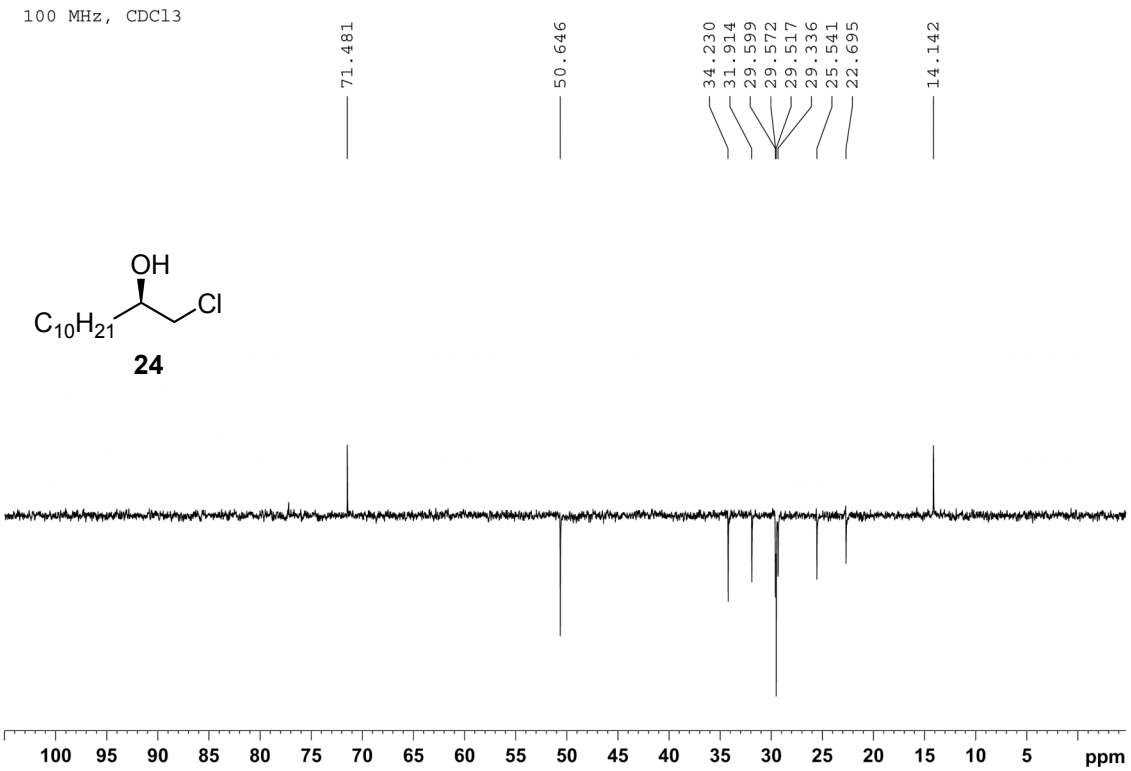
^{13}C NMR of bromochloride **14** showing chlorine- and bromine-induced isotopic shifts



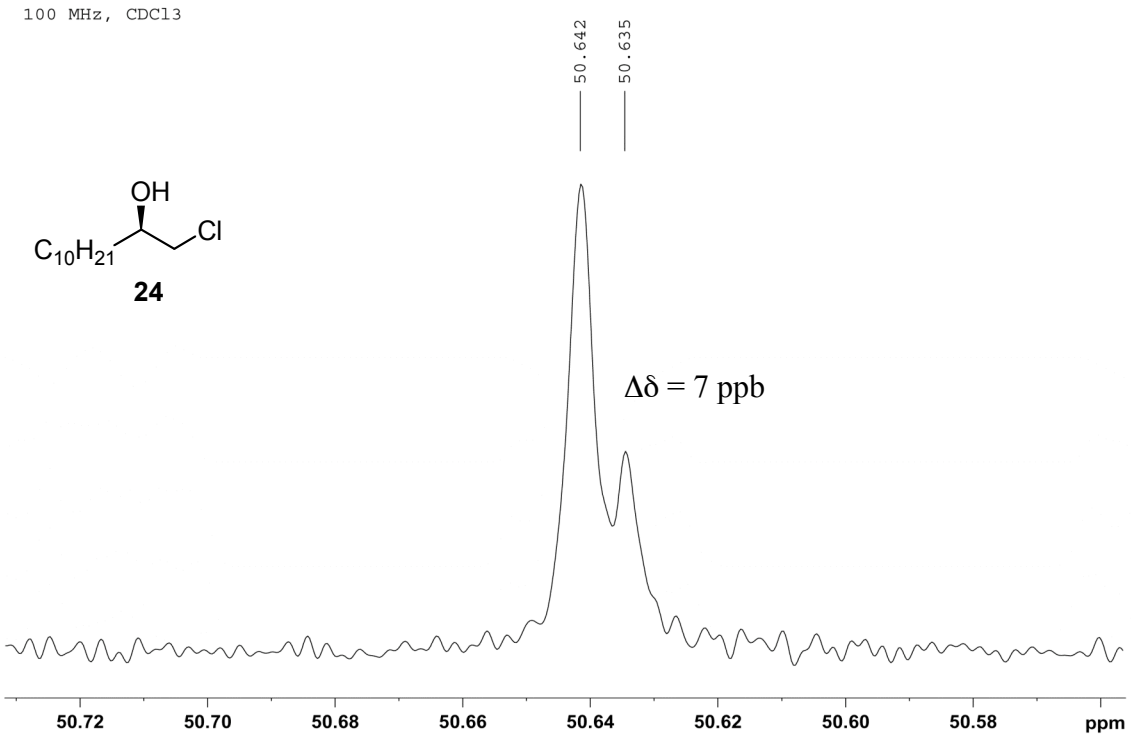
DEPT 135 spectrum of chlorohydrin **23** (CH_2 negative)



^{13}C NMR of chlorohydrin **23** showing chlorine-induced isotopic shift



DEPT 135 spectrum of chlorohydrin **24** (CH_2 negative)



^{13}C NMR of chlorohydrin **24** showing chlorine-induced isotopic shift

X-ray crystallographic details for **4** and **11**

Crystal data for **4**: C_8H_8BrCl, M = 219.50, orthorhombic, Pccn (no. 56), a = 15.6605(4), b = 19.4998(5), c = 5.49619(11) Å, V = 1678.41(7) Å^3, Z = 8, D_c = 1.737 g cm^{-3}, μ(Mo-Kα) = 5.136 mm^{-1}, T = 173(2) K, colourless plates, Oxford Diffraction Xcalibur 3 diffractometer; 23570 measured reflections, 2738 independent reflections (R_{int} = 0.0508), F^2 refinement, R_1 = 0.038, wR_2 = 0.087, 1471 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 64°], 118 parameters. CCDC 702696.

Crystal data for **11**: $C_9H_{10}BrCl$, M = 233.53, monoclinic, I2/a (no. 15), a = 18.7196(5), b = 5.4883(1), c = 19.2225(5) Å, β = 104.159(3)°, V = 1914.90(8) Å^3, Z = 8, D_c = 1.620 g cm^{-3}, μ(Cu-Kα) = 7.877 mm^{-1}, T = 173(2) K, colourless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3799 measured reflections, 1508 independent reflections reflections (R_{int} = 0.0188), F^2 refinement, R_1 = 0.028, wR_2 = 0.075, 1270 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 126°], 131 parameters. CCDC 702697.

The crystal structure of **4** is substantially disordered (in fact, there are no ordered atoms), and the best model for the electron density involves presence of two different molecules. The major occupancy molecule, **4**-A, has a chlorine on C(7) and a bromine on C(8) (ca. 84% occupancy, Fig. 1 in the paper and Fig. S1 here). The minor occupancy molecule, 4-B, has the halogens swapped, with a bromine on C(7') and a chlorine on C(8') (ca. 16% occupancy, Figs. S2 and S3). An overlay of these two molecules is shown in Fig. S4. All of the non-hydrogen atoms of the major occupancy molecule, and the halogens of the minor occupancy molecule, were refined anisotropically, all the rest isotropically. Because of the disorder a number of restraints were applied to the refinements. The C_6 rings of both molecules were constrained to be perfect hexagons with a C–C distance of 1.39 Å. The C(7) and C(7') atoms were restrained to be coplanar with their associated C_6 rings, and the C(1)–C(7) and C(1')–C(7') distances were restrained to be the same between the two species. The C(7)···C(2) and C(7)···C(6)

distances, together with their counterparts in the second molecule, were restrained to be the same. For the C_2H_3BrCl portions of the two species, the roughly equivalent bonds and angles were restrained to be the same ("roughly" because strictly speaking, for example, C(7)–Cl and C(8')–Cl' are not chemically identical, but with so much disorder around this difference is not significant and so the bonds were treated as being the same. For the thermal parameters, atoms occupying nearly the same spatial position were restrained to have similar thermal isotropic or equivalent isotropic thermal parameters.

Similar to the situation seen for the structure of **4** (see above), the crystal structure of **11** is also substantially disordered (again there are no ordered atoms), but here the two molecules present are chemically the same (they are enantiomers of each other). The major occupancy molecule, **11**-A (ca. 58% occupancy), Fig. S5 here, whilst the minor occupancy molecule, **11**-B (ca. 42% occupancy), is shown in Figs. S6 and S7). An overlay of these two molecules is shown in Fig. S8. All of the non-hydrogen atoms of the major occupancy molecule, and the halogens of the minor occupancy molecule, were refined anisotropically, all the rest isotropically. Because of the disorder a number of restraints were applied to the refinements. The C_6 rings of both molecules were constrained to be perfect hexagons with a C–C distance of 1.39 Å. The C(1) and C(1') atoms were restrained to be coplanar with their associated C_6 rings, and the C(1)–C(4) and C(1')–C(4') distances were restrained to be the same between the two species. For the C_3H_5BrCl portions of the two species, the equivalent bonds and angles were restrained to be the same, and in this case it was found to be necessary to use explicit "ideal" distances for the C–Cl (1.81 Å) and C–Br (1.97 Å) bonds (value derived from literature searches). Thermal parameter restraints were not found to be necessary, and so none were used.

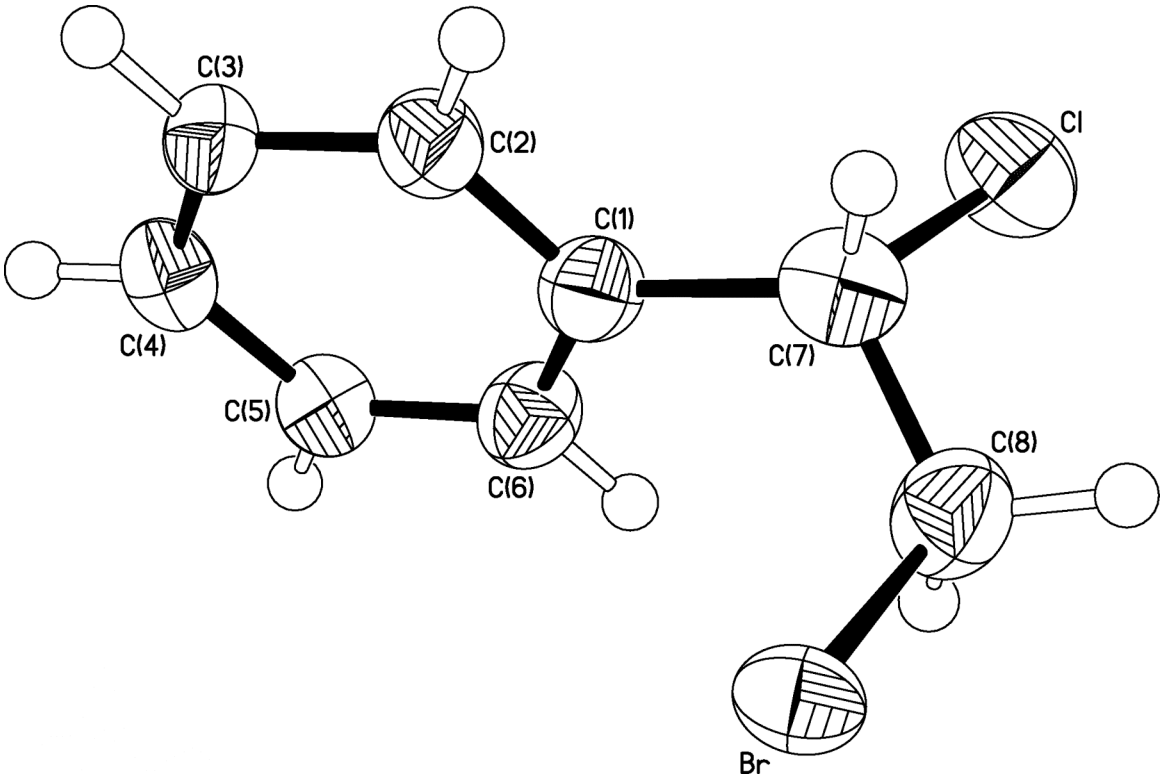


Fig. S1. The molecular structure of **4**-A, the major occupancy molecule present in the crystals of **4** (50% probability ellipsoids).

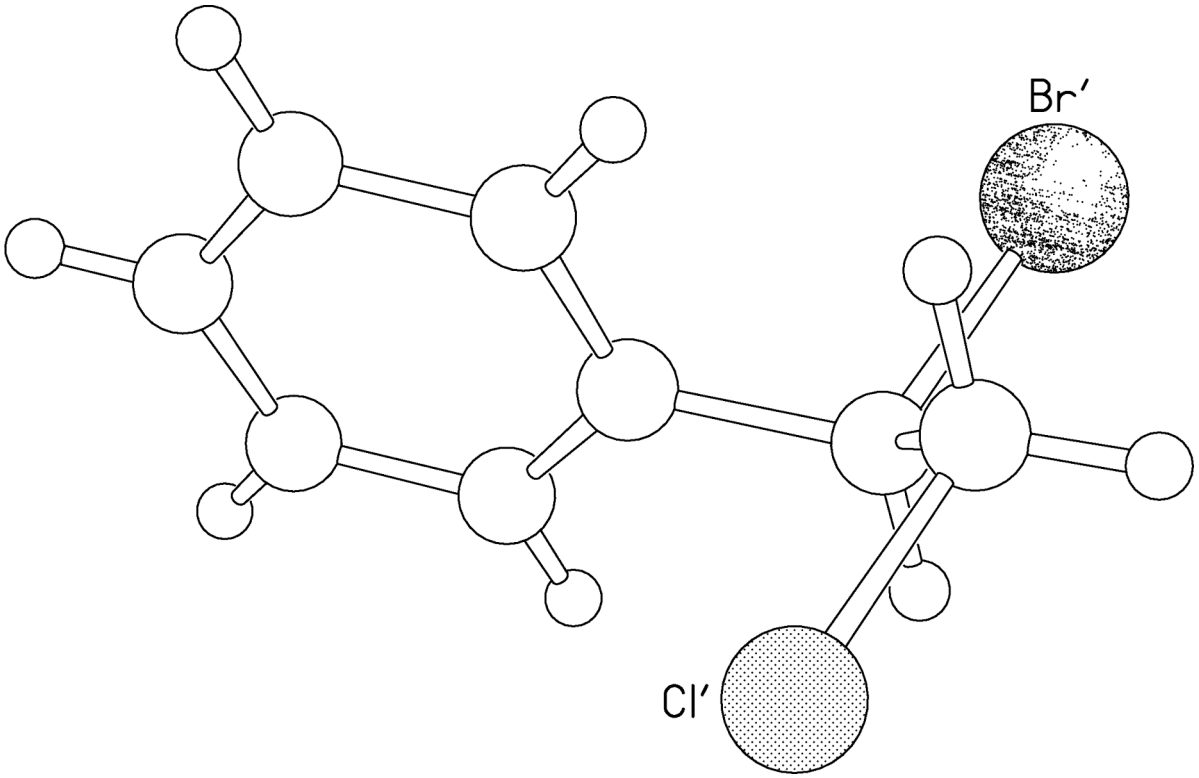


Fig. S2. The molecular structure of **4**-B, the minor occupancy molecule present in the crystals of **4**.

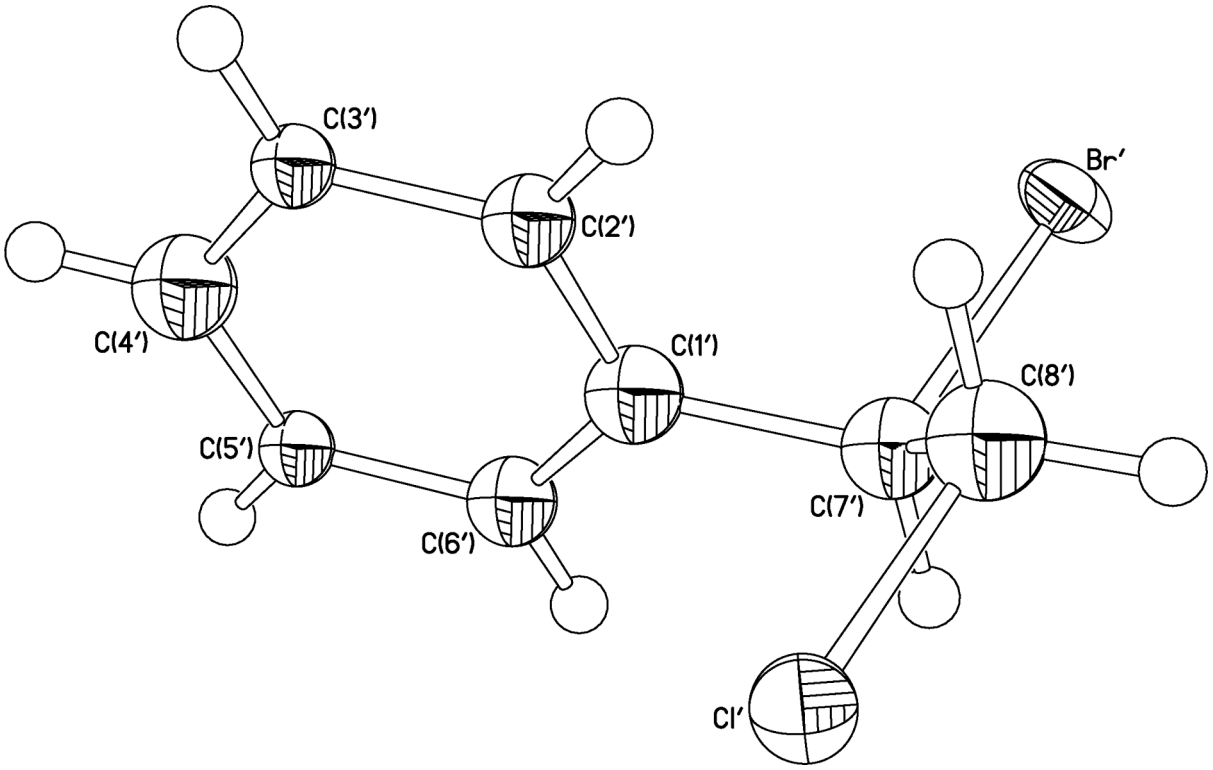


Fig. S3. The molecular structure of **4**-B, the minor occupancy molecule present in the crystals of **4** (50% probability ellipsoids).

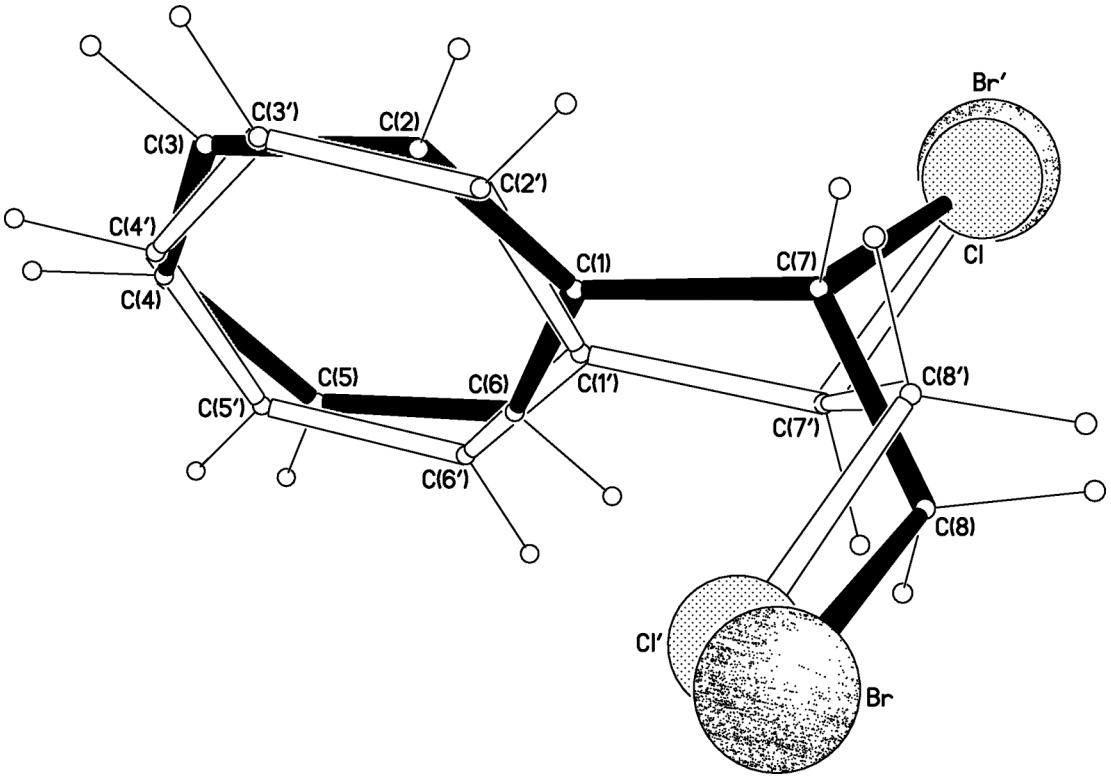


Fig. S4. Overlay of **4**-A and **4**-B, the major and minor occupancy molecules present in the crystals of **4** respectively.

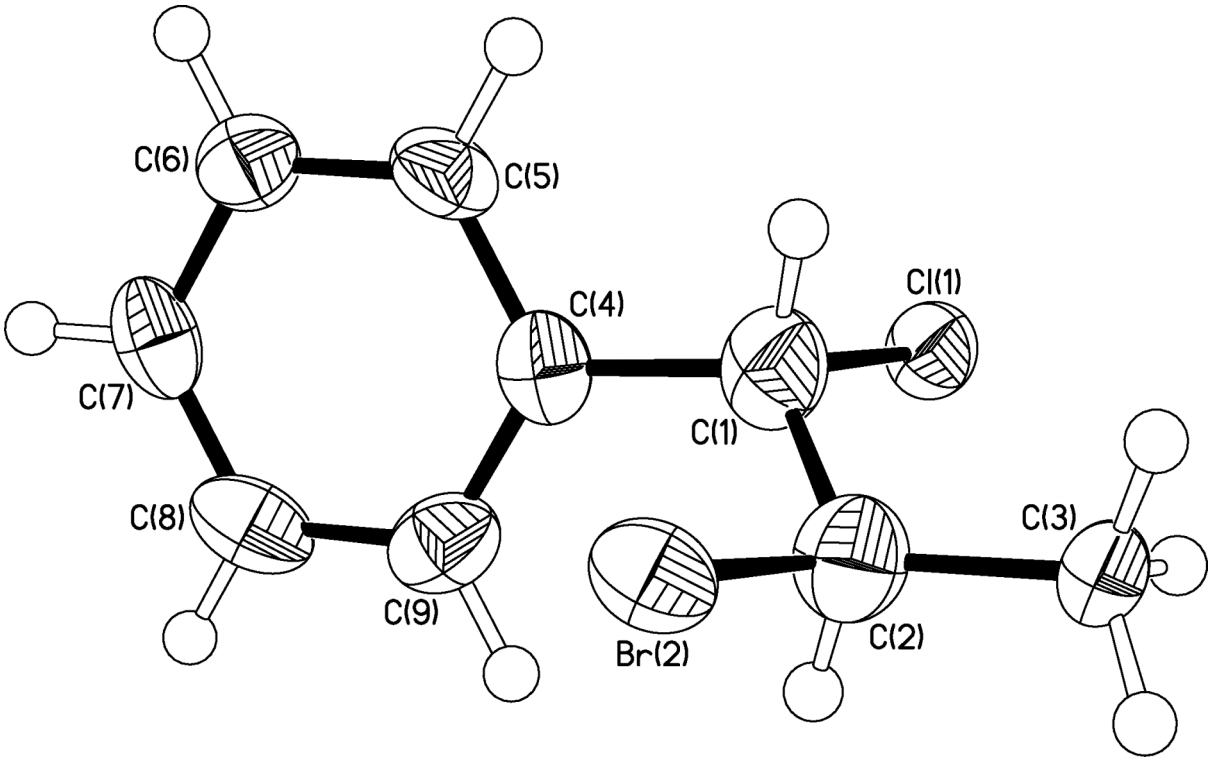


Fig. S5. The molecular structure of **11**-A, the major occupancy molecule present in the crystals of **11** (50% probability ellipsoids).

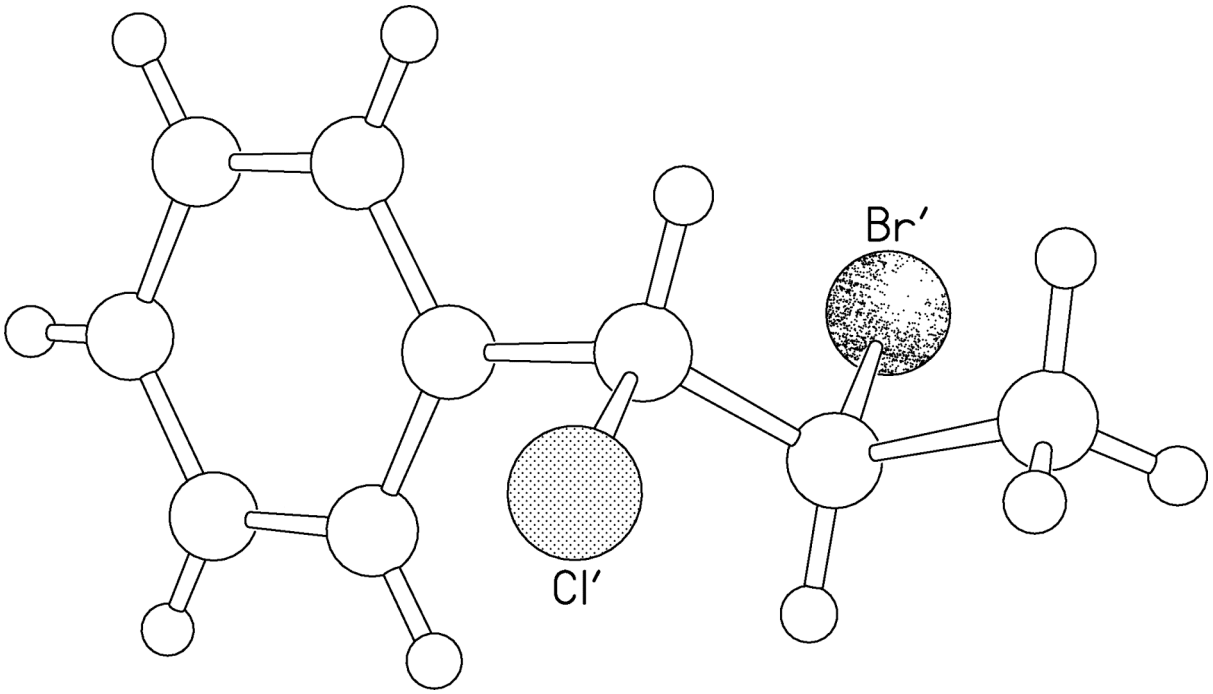


Fig. S6. The molecular structure of **11**-B, the minor occupancy molecule present in the crystals of **11**.

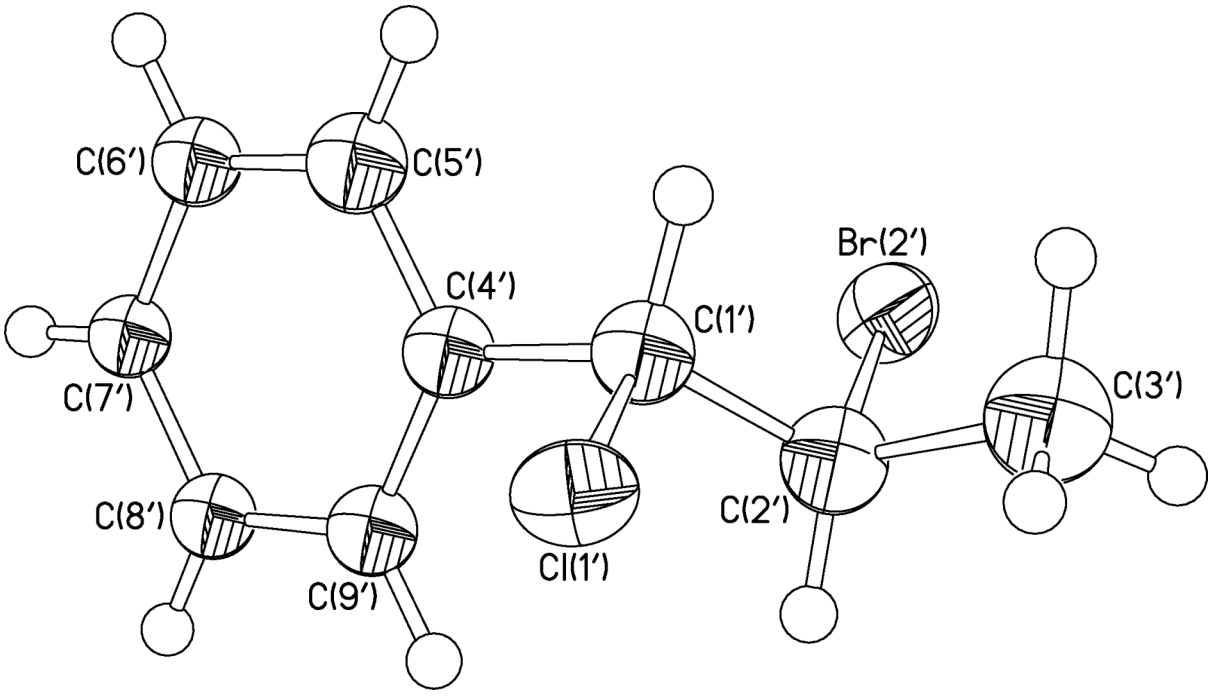


Fig. S7. The molecular structure of **11**-B, the minor occupancy molecule present in the crystals of **11** (50% probability ellipsoids).

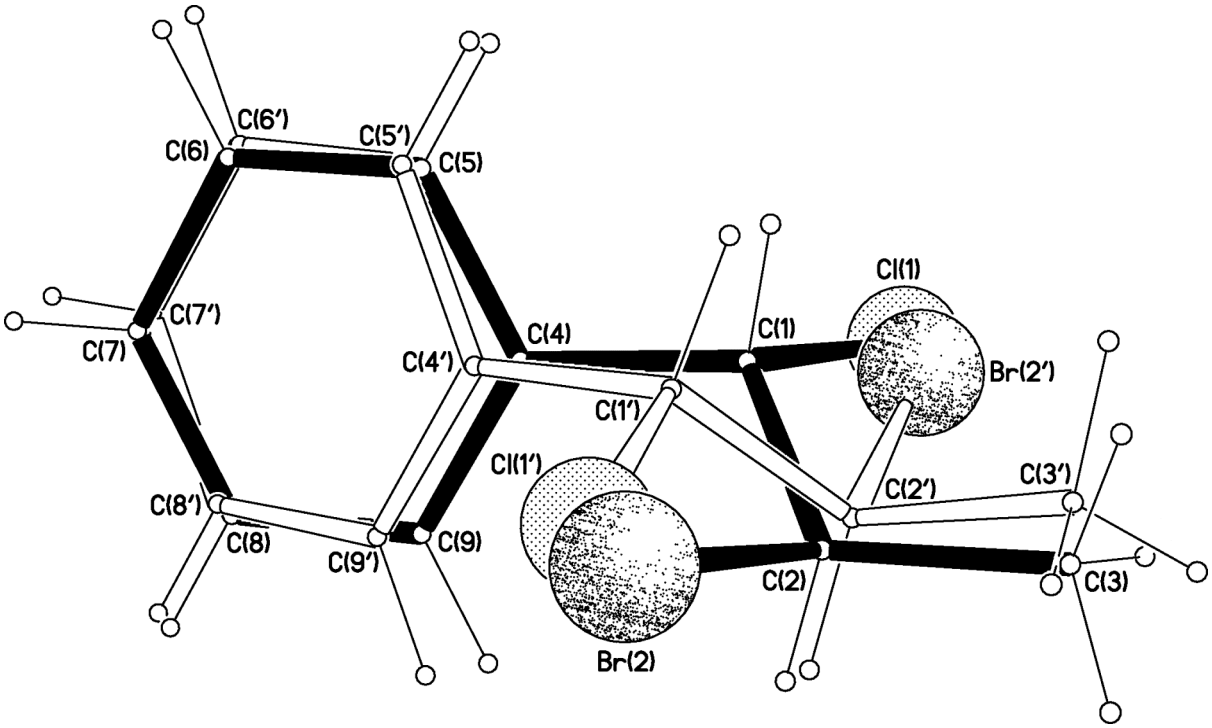


Fig. S8. Overlay of **11**-A and **11**-B, the major and minor occupancy molecules present in the crystals of **11** respectively.