Supplementary Information

Electrochemical Bromofunctionalization of Alkenes in a Flow Reactor

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General Information

Solvents and reagents were used as provided by suppliers (Sigma Aldrich, Alfa Aesar, Acros Organic, VWR and FluoroChem) without further purification or drying. 2-(pent-4-en-1-yl)isoindoline-1,3-dione was prepared according to literature.[1]

Thin layer chromatography was performed on pre-coated aluminium sheets of Merck silica gel 60 F254 (0.20 mm) and visualized by UV radiation (254 nm) or by staining with cerium ammonium molybdate solution. Flash column chromatography was performed on Biotage® Isolera Four using Biotage® cartridges SNAP Ultra 10 g or 25 g and Biotage® cartridges Sfär 10 g or 25 g. Non-UV-visible compounds were separated by manual flash chromatography using silica gel (Sigma-Aldrich, technical grade, pore size 60 Å, 230-400 mesh particle size, 40-63 µm particle size).

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker Fourier 300 apparatus and referenced relative to the residual solvent peaks (^{1}H: CDCl3, δ 7.26 ppm; ^{13}C: CDCl3, δ 77.2 ppm). The chemical shifts δ values are given in parts per million (ppm). The multiplicity of the signals was declared as followed: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, hep = septet, dd = doublet of doublets, m = multiplet, b = broad; and coupling constants (J) in Hertz.

Infrared spectroscopy was conducted with a Shimadzu FTIR Affinity-1S apparatus. Wavenumbers are quoted in cm–1. All compounds were measured neat directly on the crystal of the IR machine.

Melting points were measured using a Gallenkamp variable heater with samples in open capillary tubes.

Mass spectrometry was performed by Cardiff University Analytical Service on a Water LCR Premier XE-TOF mass spectrometer. Ions were generated by Electron Ionisation (EI) and Chemical Ionisation (CI).

Batch electrochemical experiments were carried out with an Electrasyn 2.0 device. Graphite (5cm x 0.8cm x 0.2 cm) and platinum foil (5cm x 0.5 cm) electrodes from IKA were used in 5 mL or 10 mL Electrasyn vials and immersed 3 cm deep into the solution.

Flow electrochemical experiments were carried out with an Ion electrochemical reactor from Vapourtec Ltd. KR Analytical Ltd Fusion 100 Touch syringe pumps were used in flow set-ups. GW Instek PSU 300-5 was used as power supplz Following electrodes (5 x 5 cm) were used in the ion electrochemical reactor separated by a 0.5 mm thick FEP spacer resulting in a reactor volume of 600 µL and exposed surface area of 12 cm^2: Graphite, Platinum foil (Goodfellow); Platinum plated on niobium, Platinum coated on titanium, Nickel, Glassy Carbon (GC), Panasonic carbon (Vapourtec Ltd).

General Procedures

Method A (Bromohydroxylation): The electrolysis was performed in an undivided cell using a Vapourtec ion electrochemical flow reactor (500 µm FEP spacer, 600 µL reactor volume), a platinum on niobium plate electrode as the cathode and a graphite electrode as the anode (immersed surface area: 12 cm^2 each). A solution of styrene (1 eq., 100 mM, 1 mmol, 114.5 µL) and 48% hydrobromic acid (1.8 eq., 180 mM, 1.8 mmol, 205 µL) in 10 mL of a 7:3 mixture of acetonitrile and water was pumped with a syringe pump at a flow rate of 0.2 mL/min into the ion electrochemical reactor. A constant current of 129 mA (4 F/mol) was applied. After reaching the steady state (2.5 reactor volumes, 1.5 mL, 7.5 min), the reaction mixture was collected for 35 min (7 mL). The reaction mixture was quenched with aqueous $Na_2S_2O_3$ solution and acetonitrile was removed *in vacuo*. The aqueous phase was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine (50 mL) dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (EtOAc/Petroleum ether).

Method A was adapted in certain cases to overcome solubility issues by exchanging MeCN for THF.

Method B (Bromohydroxylation): The electrolysis was performed in an undivided cell using a Vapourtec ion electrochemical flow reactor (500 µm FEP spacer, 600 µLreactor volume), a platinum plate electrode as the cathode and a graphite electrode as the anode (immersed surface area: 12 cm^2 each). A solution of styrene (1 eq., 100 mM, 1 mmol, 114.5 µL) and 48% hydrobromic acid (1.8 eq., 180 mM, 1.8 mmol, 205 µL) in 10 mL of a 7:3 mixture of acetonitrile and water was pumped with a syringe pump at a flow rate of 0.4 mL/min into the ion electrochemical reactor. A constant current of 193 mA (3 F/mol) was applied. After reaching the steady state (2.5 reactor volumes, 1.5 mL, 3.75 min), the reaction mixture was collected for 17.5 min (7 mL). The reaction mixture was quenched with aqueous $Na_2S_2O_3$ solution and acetonitrile was removed *in vacuo*. The aqueous phase was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine (50 mL) dried over $MgSO_4$ and the

solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (EtOAc/Petroleum ether).

Method B was adapted in as certain cases to overcome solubility issues by exchanging MeCN for THF.

Method C (Bromohydroxylation): The electrolysis was performed in an undivided cell using a Vapourtec ion electrochemical flow reactor (500 µm FEP spacer, 600 µL reactor volume), graphite electrodes for cathode and anode (immersed surface area: 12 cm^2 each). A solution of styrene (1 eq., 100 mM, 1 mmol, 114.5 µL) and 48% hydrobromic acid (1.8 eq., 180 mM, 1.8 mmol, 205 µL) in 10 mL of a 7:3 mixture of acetonitrile and water was pumped with a syringe pump at a flow rate of 0.2 mL/min into the ion electrochemical reactor. A constant current of 129 mA (4 F/mol) was applied. After reaching the steady state (2.5 reactor volumes, 1.5 mL, 7.5 min), the reaction mixture was collected for 35 min (7 mL). The reaction mixture was quenched with aqueous $Na_2S_2O_3$ solution and acetonitrile was removed *in vacuo*. The aqueous phase was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine (50 mL) dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (EtOAc/Petroleum ether).

Method D (Dibromination): The electrolysis was performed in an undivided cell using a Vapourtec ion electrochemical flow reactor (500 µm FEP spacer, 600 µLreactor volume), a platinum on titanium electrode (Vapourtec) as the cathode and a graphite electrode as the anode (immersed surface area: 12 cm^2 each). A solution of styrene (1 eq., 100 mM, 1 mmol, 114.5 µL) and 48% hydrobromic acid (6 eq., 600 mM, 6 mmol, 684 µL) in 10 mL of acetonitrile was pumped with a syringe pump at a flow rate of 0.4 mL/min into the ion electrochemical reactor. A constant current of 257 mA (4 F/mol) was applied. After reaching the steady state (2.5 reactor volumes, 1.5 mL, 3.75 min), the reaction mixture was collected for 17.5 min (7 mL). The reaction mixture was quenched with aqueous $Na_2S_2O_3$ solution and acetonitrile was removed *in vacuo*. The aqueous phase was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine (50 mL) dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (EtOAc/Petroleum ether).

Method E (Bromoalcoxylation): The electrolysis was performed in an undivided cell using a Vapourtec ion electrochemical flow reactor (500 µm FEP spacer, 600 µLreactor volume), a platinum plate electrode as the cathode and a graphite electrode as the anode (immersed surface area: 12 cm^2 each). A solution of styrene (1 eq., 100 mM, 1 mmol, 114.5 µL) and 48% hydrobromic acid (1.5 eq., 150 mM, 1.5 mmol, 171 µL) in 10 mL of a 7:3 mixture of acetonitrile and corresponding alcohol was pumped with a syringe pump at a flow rate of 0.4 mL/min into the ion electrochemical reactor. A constant current of 257 mA (4 F/mol) was applied. After reaching the steady state (2.5 reactor volumes, 1.5 mL, 3.75 min), the reaction mixture was collected for 17.5 min (7 mL). The reaction mixture was quenched with aqueous $Na_2S_2O_3$ solution and acetonitrile was removed *in vacuo*. The aqueous phase was extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine (50 mL) dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (EtOAc/Cyclohexane).

Optimization of Methods

Electrochemical Dibromination of Styrene in Batch

The conditions for the dibromination of alkenes were adapted from a batch electrochemical procedure from Aiwen Lei and co-workers.[2] The reaction was performed in a 5 mL Electrasyn vial with platinum foil cathode (surface area: 1.5 cm^2) and graphite anode (surface area: 2.4 cm^2). A current of 17 mA was applied corresponding to a current density of 7.08 mA/cm^2, which was chosen based on the exposed surface area of the graphite rod reported in the original procedure. The adapted reaction mixture consisted of styrene (46 mM), hydrobromic acid (90 mM) and *tetra*-butyl ammonium tetrafluoroborate (9.2 mM) in a mixture of 2% water in acetonitrile. The product 1,2-dibromo-1-pehenylethane (**2a**) was obtained in 44% and 46% yield compared to the reported yield of 73%.[2]

Optimization of the Bromohydroxylation of Styrene

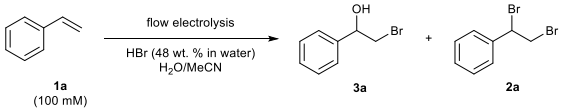


Table S1. Optimization of the water concentration in the electrochemical bromohydroxylation in flow.

Entry	additional H_2O	3a	2a
1	5%	40%	29%
2	10%	53%	30%
3	15%	63%	18%
4	20%	79%	14%
5	25%	81%	9%
6	30%	81%	7%
7	35%	66%	2%
8	40%	68%	3%

Reaction conditions: styrene (100 mM), hydrobromic acid (48% w/w in water, 200 mM); 0.2 mL/min; 3 F/mol; constant current; undivided cell; Pt foil cathode, Graphite anode (surface area: 12 cm^2); Yields are determined by NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S2. Optimization of bromide concentration in the electrochemical bromohydroxylation of alkenes in flow.

Entry	Br^- source	Br^- [mM]	additional H_2O	3a	2a
1	HBr	100	20%	31%	1%
2	HBr	150	20%	55%	4%
3	HBr	160	20%	63%	7%
4	HBr	170	20%	66%	8%
5	HBr	180	20%	85%	9%
6	HBr	190	20%	84%	13%
7[a]	HBr	180	20%	52%	13%
8[b]	HBr	180	20%	72%	5%
9	HBr	180	30%	85%	8%
10	LiBr	180	30%	6%	6%
11	NaBr	180	30%	0%	0%
12	NH_4Br	180	30%	49%	9%

Reaction conditions: styrene (100 mM); HBr:hydrobromic acid (48% w/w in water); 0.2 mL/min; 3 F/mol; constant current; undivided cell; Pt foil cathode, Graphite anode (surface area: 12 cm^2); Yields are

determined by NMR with 1,3,5-trimethoxybenzene as internal standard. a) styrene (50 mM); b) 150 (mM)

Table S3. Optimization of electrode materials in the electrochemical bromohydroxylation of alkenes in flow.

Entry	Cathode	Anode	3a	2a
1	Pt on Ti	Graphite	85%	13%
2	Ni	Graphite	75%	6%
3	Graphite	Graphite	82%	12%
4	Pt	Panasonic Carbon	67%	9%
5	Pt	Glassy Carbon	72%	6%
6	Pt	Pt	2%	25%
7	Graphite	Pt	75%	14%

Reaction conditions: styrene (100 mM), hydrobromic acid (48% w/w in water, 180 mM); additional H_2O/MeCN 2:8; 0.2 mL/min; 3 F/mol; constant current; undivided cell; working electrode (surface area: 12 cm^2); Pt on Ti: Platinum coated on titanium; Ni: Nickel foil; Yields are determined by NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S4. Optimization of charge and flow rate in the electrochemical bomohydroxylation in flow.

Entry	Charge [F/mol]	Flow rate [mL/min]	3a	2a
1	2	0.2	63	9
2	4	0.2	86	4
3	5	0.2	68	3
4	3	0.4	81	7
5	4	0.4	75	6
6	3	0.6	72	6
7	4	0.6	70	6

Reaction conditions: styrene (100 mM), hydrobromic acid (48% w/w in water, 180 mM); additional H_2O/MeCN 3:7; constant current; undivided cell; Pt foil cathode, Graphite anode (surface area: 12 cm^2); Yields are determined by NMR with 1,3,5-trimethoxybenzene as internal standard.

Scale-up Test for the Bromohydroxylation of Styrene

The yield of the electrochemical bromohydroxylation was tracked over a period of 3h 50min. The optimized reaction conditions (method A) were used. Aliquots of 1 mL (5 min) were collected in 30 min intervals and internal standard 1,3,5-trimethoxybenzene was added to determine the yield by ^{1}H-NMR.

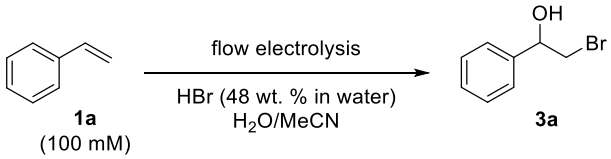


Table S5. Scale-up experiment for Bromohydroxylation of Styrene.

Entry	time	3a [%]
1	0min	67
2	30min	71
3	1h 00min	67
4	1h 30min	65
5	2h 00min	67

6	2h 30min	65
7	3h 30min	69
8	3h 45min	68

Reaction conditions: styrene (100 mM), hydrobromic acid (180 mM); H_2O/MeCN 3:7; constant current; undivided cell; Pt coated on Nb cathode, Graphite anode (surface area: 12 cm^2); Reactor volume: 600 µL; 500 µm spacer; Yields were determined by NMR with 1,3,5-trimethoxybenzene as internal standard.

Scale-up for the Dibromination of Styrene

When scaling up the dibromination of styrene to 21.8 mmol (9.1 h or 545.5 min, 0.4 mL/min), **2a** was obtained in only 47 % yield (2.698 g, 10.22 mmol) while 1.41 g of a yellow liquid consisting of 2-bromo-1-phenylethanol (**3a**) and 1-phenylethanol (**3a'**) was obtained as side products. In a control experiment the reaction mixture consisting of styrene (0.1 M) and hydrobromic acid (48% w/w in water, 0.6 M) in 5 mL of acetonitrile was stirred at room temperature. After 8.5 h, 1-phenylethanol could be observed in 21% NMR-yield. This side product could arise from the acid catalyzed hydration of the alkene, which takes place in the reservoir.

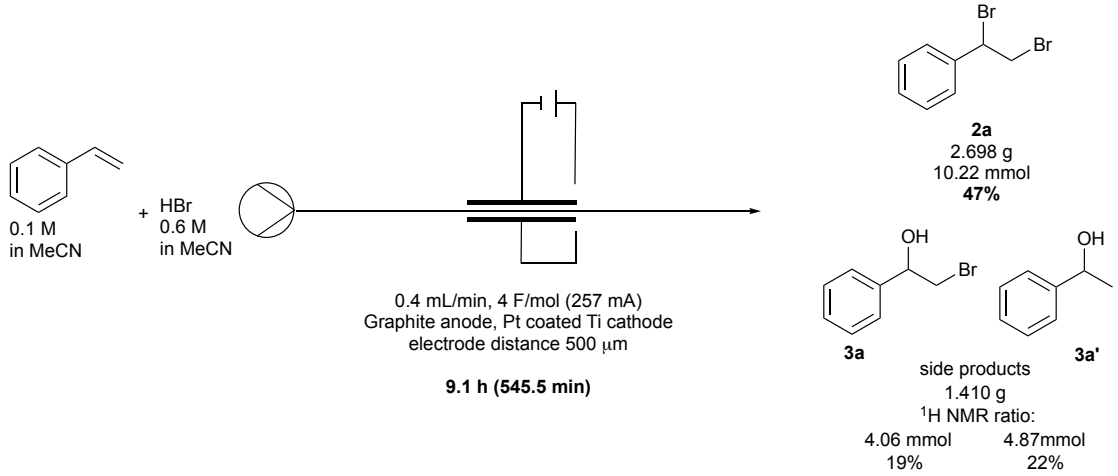
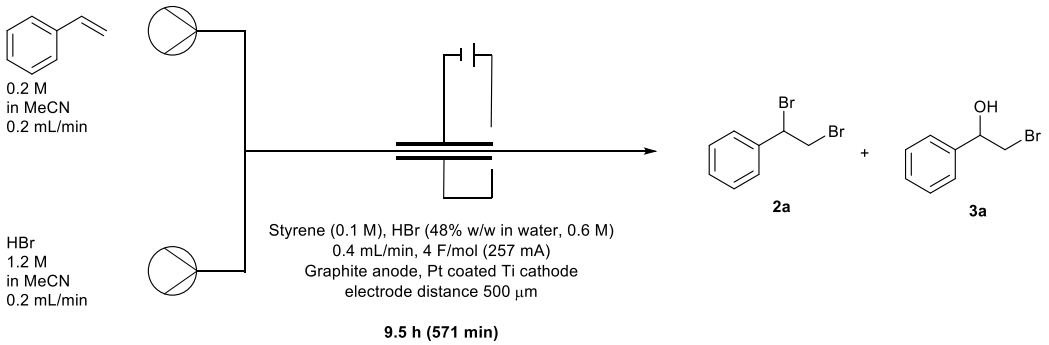


Figure S1: Large scale dibromination of styrene in flow with premixing of reactants in one reservoir.

This limitation was overcome by separating the reactants before entering the reactor:The electrolysis was performed in an undivided cell using a Vapourtec ion electrochemical flow reactor (500 µm FEP spacer, 600 µLreactor volume), a platinum on titanium electrode (Vapourtec) as the cathode and a graphite electrode as the anode (immersed surface area: 12 cm^2 each). A solution of styrene (1 eq., 200 mM, 23 mmol, 2.64 mL) in 115 mL of acetonitrile and a solution of hydrobromic acid (48% w/w in water, 6 eq., 600 mM, 6 mmol, 15.7 mL) in 115 mL of acetonitrile were pumped with a syringe pump at a flow rate of 0.2 mL/min each. The solutions were mixed with a ratio of 1:1 in a T-piece before entering the Ion Electrochemical Reactor. A constant current of 257 mA (4 F/mol, styrene concentration in the reactor: 100 mM) was applied. After reaching the steady state (2.5 reactor volumes, 1.5 mL, 3.75 min), the reaction mixture was collected for 571 min (228.4 mL). The reaction mixture was quenched with aqueous NaS_2O_3 solution and acetonitrile was removed *in vacuo*. After removal of acetonitrile and neutralization with $NaHCO_3$, the pure product was obtained by filtration and drying as 3.934 g of a white solid (65%, 14.90 mmol). The productivity of the large scale experiment was calculated to be 413 mg/h.

Aliquots of 0.4 mL reaction mixture were taken afte 0 h, 3.5 h, 7 h and 9.5 h and were analyzed by ^{1}H-NMR to monitor the reaction (Table S6).

Table S6: Monitoring of the Scale-upexperiment for Dibromination of Styrene

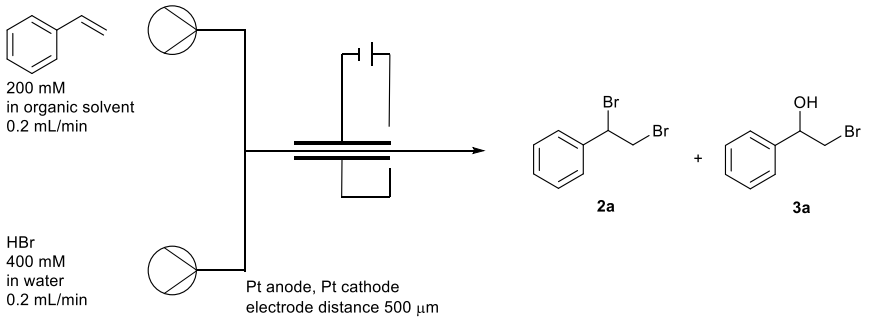


Entry	time	2a [%]	3a [%]
1	0h 0min	87	15
2	3h 36 min	83	12
3	6h 48min	74	12
4	9h 26min	76	13

Electrochemical dibromination of alkenes in flow. Reaction conditions: styrene (0.1 M), hydrobromic acid (0.6 M); MeCN; 0.4 mL/min, 4 F/mol; constant current; undivided cell; Graphite anode (surface area: 12 cm^2); Pt coated Ti cathod; Reactor volume: 600 µL; 500 µm spacer; Yields were determined by NMR with 1,3,5-trimethoxybenzene as internal standard.

Effects of Co-solvent on Selectivity

The interactions of different organic co-solvents with water were tested regarding the selectivity for the dibromination or bromohydroxylation of styrene. The highest yields for **2a** were observed with methyl tertbutyl ether while the highest selectivity was achieved with dichloromethane. Dimethyl sulfoxide and acetonitrile gave the highest yield and selectivity for product **3a**.

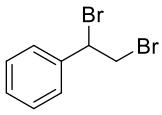


Entry	Organic Solvent	Dibromide	Bromohydrin
1	Dimethyl sulfoxide	1%	64%
2	Acetonitrile	4%	60%
3	Tetrahydro furane	10%	53%
4	Ethyl acetate	31%	29%
5	Diethyl ether	48%	18%
6	Methyl tertbutyl ether	56%	19%
7	Dichloromethane	46%	7%
8	Chloroform	36%	11%
9	Toluene	34%	8%
10	Cyclohexane	22%	15%
11	n-Pentane	27%	17%

Solution 1: 400mM HBr in water, 0.2 mL/min; Solution 2: 200 mM styrene in solvent, 0.2 mL/min; Solution 1 and 2 were joined via a T-piece before entering the reactor; Reactor: Platinum anode and cathode, 2 F/mol, 500µm FEP spacer (600µL reactor volume).

Characterization of Products

(1,2-Dibromoethyl)benzene (2a)



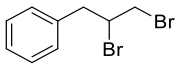
The product was obtained from styrene (0.66 mmol) as a white solid (86%, 150 mg, 0.57 mmol) by using method D. The spectral data are in agreement with the literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.29 (m, 5H), 5.15 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.13 – 3.97 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 129.3, 129.0, 127.8, 51.0, 35.1.

MP: 72-74 °C.

(2,3-Dibromopropyl)benzene (2b)

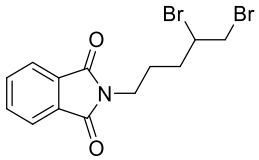


The product was obtained from allylbenzene (0.64 mmol) as a white solid (64%, 114 mg, 0.41 mmol) by using method D. The spectral data are in agreement with the literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 4.43 – 4.30 (m, 1H), 3.83 (dd, *J* = 10.5, 4.2 Hz, 1H), 3.63 (dd, *J* = 10.5, 9.0 Hz, 1H), 3.51 (dd, *J* = 14.5, 4.8 Hz, 1H), 3.13 (dd, *J* = 14.5, 7.8 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 129.7, 128.7, 127.4, 52.6, 42.1, 36.2.

2-(4,5-Dibromopentyl)isoindoline-1,3-dione (2c)



The product was obtained from 2-(pent-4-en-1-yl)isoindoline-1,3-dione (0.7 mmol) as a white viscous oil (84%, 221 mg, 0.59 mmol) by using method D.

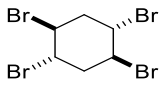
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.20 (ddd, *J* = 12.9, 9.0, 4.2 Hz, 1H), 3.82 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.73 (t, *J* = 6.7 Hz, 2H), 3.59 (t, *J* = 10.0 Hz, 1H), 2.29 – 2.09 (m, 1H), 2.09 – 1.91 (m, 1H), 1.91 – 1.74 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 134.1, 132.1, 123.4, 51.9, 37.1, 36.1, 33.3, 26.2.

HRMS (EI+) *m/z*: calcd. for $[M]^+$ ($C_{13}H_{14}O_2N^{79}Br$): 373.93858; found: 373.9385.

IR ν_{max}/cm^{-1} (neat): 2936, 1771, 1701, 1614, 1466, 1435, 1395, 1364, 1188, 1020, 885, 716, 569, 529.

(1S,2S,4S,5S)-1,2,4,5-Tetrabromocyclohexane (2d)



The product was obtained from 1,4-cyclohexadiene (0.7 mmol) as a white solid (34 %, 95 mg, 0.24 mmol) by using method D. (4R,5R)-4,5-dibromocyclohex-1-ene was observed as minor product in the crude ^{1}H-NMR but could not be isolated in pure form.

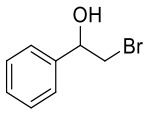
The spectral data are in agreement with the literature.[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.65 – 4.34 (m, 4H), 2.88 (bs, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 50.8, 39.9.

MP: 190-192 °C.

2-Bromo-1-phenylethan-1-ol (3a)



The product was obtained from styrene (0.68 mmol) as a colourless oil (81%, 111 mg, 0.55 mmol) by using method A with platinum foil instead of platinum on niobium as the cathode.

The product was obtained from styrene (0.7 mmol) as a colourless oil (77%, 108 mg, 0.54 mmol) by using method A.

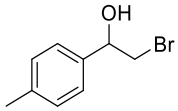
The product was obtained from styrene (0.5 mmol) as a colourless oil (78%, 78 mg, 0.39 mmol) by using method C.

The spectral data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 4.93 (dd, *J* = 8.9, 3.4 Hz, 1H), 3.65 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.55 (dd, *J* = 10.5, 9.0 Hz, 1H), 2.64 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 128.8, 128.6, 126.1, 73.9, 40.3 ppm.

2-Bromo-1-(p-tolyl)ethan-1-ol (3b)



The product was obtained from 4-methylstyrene (0.66 mmol) as a yellow oil (76%, 108 mg, 0.50 mmol) by using method A. Platinum foil was used instead of platinum on niobium as the cathode.

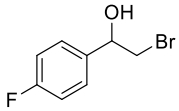
The product was obtained from 4-methylstyrene (0.5 mmol) as a yellow oil (61%, 66 mg, 0.31 mmol) by using method C.

The spectral data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.90 (d, *J* = 9.0 Hz, 1H), 3.63 (dd, *J* = 10.4, 3.5 Hz, 1H), 3.54 (dd, *J* = 10.4, 8.9 Hz, 1H), 2.57 (d, *J* = 2.6 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 137.4, 129.5, 126.0, 73.8, 40.4, 21.3.

2-Bromo-1-(4-fluorophenyl)ethan-1-ol (3c)



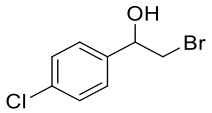
The product was obtained from 4-fluorostyrene (0.73 mmol) as a colourless oil (83%, 133 mg, 0.61 mmol) by using method A. The spectral data are in agreement with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.12 – 7.02 (m, 2H), 4.92 (dt, *J* = 8.8, 3.2 Hz, 1H), 3.62 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.51 (dd, *J* = 10.5, 8.9 Hz, 1H), 2.63 (d, *J* = 3.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7 (d, *J* = 246.9 Hz), 136.2 (d, *J* = 3.0 Hz), 127.8 (d, *J* = 8.2 Hz), 115.7 (d, *J* = 21.6 Hz), 73.2, 40.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.43 (tt, *J* = 8.9, 5.3 Hz).

2-Bromo-1-(4-chlorophenyl)ethan-1-ol (3d)



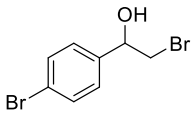
The product was obtained from 4-chlorostyrene (1.03 mmol) as a white solid (68%, 164 mg, 0.70 mmol) by using method B. Platinum on niobium was used instead of platinum foil. The spectral data are in agreement with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 4.91 (dt, *J* = 8.8, 3.3 Hz, 1H), 3.62 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.50 (dd, *J* = 10.5, 8.8 Hz, 1H), 2.62 (d, *J* = 3.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 134.3, 128.9, 127.5, 73.1, 39.9.

MP: 59-61 °C.

2-Bromo-1-(4-bromophenyl)ethan-1-ol (3e)



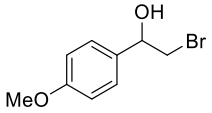
The product was obtained from 4-bromostyrene (0.72 mmol) as a white solid (71%, 144 mg, 0.51 mmol) by using method A. The spectral data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.31 – 7.24 (m, 2H), 4.90 (dt, *J* = 8.7, 3.3 Hz, 1H), 3.62 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.50 (dd, *J* = 10.5, 8.8 Hz, 1H), 2.63 (d, *J* = 3.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 131.9, 127.8, 122.5, 73.2, 40.0.

MP: 69-72 °C.

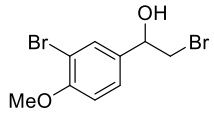
2-Bromo-1-(4-methoxyphenyl)ethan-1-ol (3f)



The product was obtained from 4-bromostyrene (0.72 mmol) as a white solid (66%, 109 mg, 0.47 mmol) by using method A. The spectral data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 6.93 – 6.86 (m, 2H), 4.87 (dd, *J* = 8.7, 3.7 Hz, 1H), 3.80 (s, 3H), 3.59 (dd, *J* = 10.4, 3.7 Hz, 1H), 3.52 (dd, *J* = 10.4, 8.8 Hz, 1H), 2.70 (s, 1H).

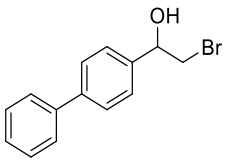
^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 132.5, 127.4, 114.2, 73.6, 55.4, 40.4 ppm.



To a small extent, bromination of the aromatic ring was observed and **2-bromo-1-(3-bromo-4-methoxyphenyl)ethan-1-ol** was isolated as the side product (29 mg, 0.09mmol, 13 %).[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.0 Hz, 1H), 7.29 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.86 (d, *J* = 8.9 Hz, 1H), 3.90 (s, 3H), 3.60 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.50 (dd, *J* = 10.5, 8.8 Hz, 1H), 2.60 (d, *J* = 2.8 Hz, 1H).

1-([1,1'-Biphenyl]-4-yl)-2-bromoethan-1-ol (3g)



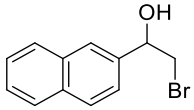
The product was obtained from 4-vinylbiphenyl (80 mM in a 3:3:4 mixture of H_2O/MeCN/THF, 0.752 mmol) as a white solid (65%, 135 mg, 0.49 mmol) by using a modified method A. The spectral data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.2, 6.5 Hz, 4H), 7.45 (t, *J* = 8.1 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 4.99 (dd, *J* = 8.9, 3.1 Hz, 1H), 3.69 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.59 (dd, *J* = 10.4, 9.0 Hz, 1H), 2.66 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 140.7, 139.3, 129.0, 127.6, 127.6, 127.3, 126.6, 73.7, 40.4.

MP: 80-83 °C.

2-Bromo-1-(naphthalen-2-yl)ethan-1-ol (3h)

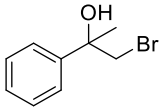


The product was obtained from 2-vinylnaphthalene (0.75 mmol) as a brown solid (54%, 101 mg, 0.40 mmol) by using a method A. The spectral data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 4H), 7.54 – 7.45 (m, 3H), 5.10 (dd, *J* = 8.8, 3.4 Hz, 1H), 3.73 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.63 (dd, *J* = 10.5, 8.9 Hz, 1H), 2.73 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 133.4, 133.3, 128.7, 128.2, 127.9, 126.6, 126.4, 125.3, 123.7, 74.0, 40.3.

1-Bromo-2-phenylpropan-2-ol (3i)

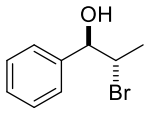


The product was obtained from α-methylstyene (0.7 mmol) as a yellow oil (48%, 73 mg, 0.34 mmol) by using a method B. The spectral data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.42 – 7.34 (m, 2H), 7.34 – 7.26 (m, 1H), 3.77 (d, *J* = 10.4 Hz, 1H), 3.71 (d, *J* = 10.4 Hz, 1H), 2.55 (s, 1H), 1.69 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 128.6, 127.7, 125.0, 73.3, 46.4, 28.2.

2-Bromo-1-phenylpropan-1-ol (3j)



The product was obtained from trans-β-methylstyene (0.7 mmol) as a yellow oil (74%, 111 mg, 0.52 mmol, dr >20:1) by using a method B.

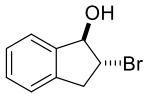
The product was obtained from trans-β-methylstyene (0.5 mmol) as a yellow oil (45%, 48 mg, 0.22 mmol, dr >20:1) by using a method C.

The spectral data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 5.02 (d, *J* = 3.1 Hz, 1H), 4.44 (qd, *J* = 6.8, 3.5 Hz, 1H), 2.47 (s, 1H), 1.55 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 128.5, 128.2, 126.5, 77.4, 56.3, 18.9.

2-Bromo-2,3-dihydro-1H-inden-1-ol (3k)



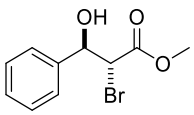
The product was obtained from indene (100 mM in a 3:7 mixture of H_2O/THF, 0.7 mmol) as a white solid (52%, 78 mg, 0.37 mmol, dr >20:1) by using a modified method B. The spectral data are in agreement with the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 5.41 – 5.23 (m, 1H), 4.29 (dd, *J* = 13.9, 6.6 Hz, 1H), 3.58 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.22 (dd, *J* = 16.2, 7.4 Hz, 1H), 2.38 (d, *J* = 4.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 139.9, 129.1, 127.8, 124.7, 124.2, 83.5, 54.6, 40.6.

MP: 128-130 °C.

Methyl 2-bromo-3-hydroxy-3-phenylpropanoate (3l)



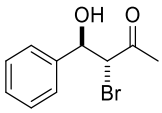
The product was obtained from methyl cinnamate (0.74 mmol) as a colourless oil (41%, 79 mg, 0.30 mmol, dr >20:1) by using method A. The spectral data are in agreement with the literature.[6]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 5H), 5.09 (d, *J* = 8.1 Hz, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 3.81 (s, 3H), 3.11 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 139.0, 129.0, 128.7, 127.1, 75.4, 53.3, 47.5.

MP: 58-60 °C.

3-Bromo-4-hydroxy-4-phenylbutan-2-one (3m)

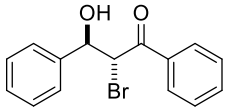


The product was obtained from trans-4-phenyl-3-buten-2-one (0.75 mmol) as a colourless oil (50%, 92 mg, 0.38 mmol, dr >20:1) by using method A. The spectral data are in agreement with the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 5H), 5.06 (d, *J* = 8.6 Hz, 1H), 4.39 (d, *J* = 8.6 Hz, 1H), 3.21 (s, 1H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 202.9, 139.3, 128.9, 128.7, 127.2, 74.9, 54.5, 27.9.

2-Bromo-3-hydroxy-1,3-diphenylpropan-1-one (3n)

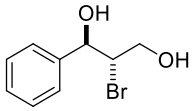


The product was obtained from trans-1,4-diphenyl-3-buten-2-one (0.74 mmol) as a yellow oil (39%, 88 mg, 0.29 mmol, dr >20:1) by using method A. The spectral data are in agreement with the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.44 (m, 4H), 7.44 – 7.31 (m, 3H), 5.35 (d, *J* = 8.3 Hz, 1H), 5.24 (d, *J* = 8.3 Hz, 1H), 3.55 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 139.5, 134.6, 134.3, 129.1, 129.0, 128.7, 128.6, 127.4, 74.9, 48.0.

2-Bromo-1-phenylpropane-1,3-diol (3o)

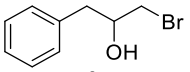


The product was obtained from cinnamyl alcohol (0.88 mmol) as a yellow oil (56%, 104 mg, 0.45 mmol, dr >20:1) by using method A. The spectral data are in agreement with the literature.[4]

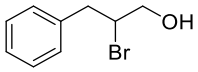
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 5H), 5.02 (dd, *J* = 6.0, 3.3 Hz, 1H), 4.27 (dd, *J* = 10.9, 4.9 Hz, 1H), 4.06 – 3.94 (m, 1H), 3.92 – 3.80 (m, 1H), 3.37 (s, 1H), 2.81 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 128.7, 128.6, 126.6, 76.9, 64.3, 59.4.

1-Bromo-3-phenylpropan-2-ol (3p) & 2-bromo-3-phenylpropan-1-ol (3p')



3p



3p'

The product was obtained from allyl benzene (0.7 mmol) as a 1.78:1.00 (**3p**/**3p'**) mixture of regioisomers (43%, 64 mg, 0.30 mmol) by using method A. Platinum foil was used instead of platinum on niobium. The separation of the regioisomers by column chromatography afforded 1-bromo-3-phenylpropan-2-ol (41 mg, 0.19 mmol, **3p**) and 2-bromo-3-phenylpropan-1-ol (23 mg, 0.11 mmol, **3p'**) as yellow oils.

The product was obtained from allyl benzene (1.48 mmol) as a 1.78:1.00 (**3p**/**3p'**) mixture of regioisomers (46%, 148 mg, 0.69 mmol) by using method B.

The spectral data are in agreement with the literature.[9,10]

1-Bromo-3-phenylpropan-2-ol (3p)

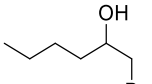
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.21 (m, 5H), 4.11 – 3.99 (m, 1H), 3.56 (dd, *J* = 10.4, 3.8 Hz, 1H), 3.42 (dd, *J* = 10.4, 6.3 Hz, 1H), 2.93 (d, *J* = 6.6 Hz, 2H), 2.20 (d, *J* = 4.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 129.5, 128.8, 127.0, 72.0, 41.5, 39.3.

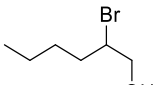
2-Bromo-3-phenylpropan-1-ol (3p')

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 5H), 4.32 (tdd, *J* = 7.4, 6.1, 3.8 Hz, 1H), 3.83 (dd, *J* = 12.3, 3.7 Hz, 1H), 3.73 (dd, *J* = 12.4, 5.9 Hz, 1H), 3.27 (dd, *J* = 14.1, 7.3 Hz, 1H), 3.17 (dd, *J* = 14.2, 7.5 Hz, 1H), 2.10 (s, 1H).

1-Bromohexan-2-ol (3q) & 2-bromohexan-1-ol (3q')



3q



3q'

The product was obtained from 1-hexene (1.44 mmol) as a 79:21 (2q/3q) mixture of regioisomers (33%, 87 mg, 0.48 mmol) by using method B. The separation of the regioisomers by column chromatography afforded pure 1-bromohexan-2-ol (63 mg, **3q**) and a mixture of 1-bromohexan-2-ol and 2-bromohexan-1-ol (4 mg, **3q**/**3q'** 1.33:1 & 20 mg, **3q**/**3q'** 1:4.56) as yellow oils. The spectral data are in agreement with the literature.[11]

1-Bromohexan-2-ol (3q)

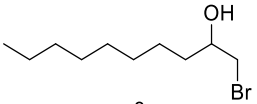
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83-3.72 (m, 1H), 3.55 (dd, *J* = 10.3, 3.2 Hz, 1H), 3.39 (dd, *J* = 10.3, 7.1 Hz, 1H), 2.09 (s, 1H), 1.60 – 1.30 (m, 6H), 0.91 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 71.2, 40.9, 34.9, 27.9, 22.7, 14.1.

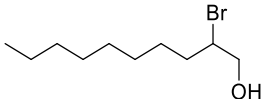
2-bromohexan-1-ol (3q')

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.15 (ddd, *J* = 13.7, 6.9, 4.0 Hz, 1H), 3.78 (qd, *J* = 12.3, 5.3 Hz, 2H), 3.55 (dd, *J* = 10.3, 3.2 Hz, 0.22 x 1H, 3q), 3.39 (dd, *J* = 10.3, 7.1 Hz, 0.21 x 1H, 3q), 2.04 (s, 1H), 1.85 –1.81 (m, 2H), 1.64 – 1.24 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H).

1-Bromodecan-2-ol (3r) & 2-bromodecan-1-ol (3r')



3r



3r'

The product was obtained from 1-hexene (1.7 mmol) as a 1:1.04 (**3r/3r'**) mixture of regioisomers (59%, 239 mg, 1.01 mmol) by using method A. The separation of the regioisomers by column chromatography afforded pure 1-bromodecan-2-ol (87 mg, **3r**) and mixtures of 1-bromodecan-2-ol and 2-bromodecan-1-ol (24 mg, **3r**/**3r'** 1.13:1 & 128 mg, **3r**/**3r'** 1:6.69) as yellow oils. The spectral data are in agreement with the literature.[12]

1-Bromodecan-2-ol (3r)

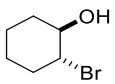
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.84 – 3.71 (m, 1H), 3.55 (dd, *J* = 10.3, 3.2 Hz, 1H), 3.38 (dd, *J* = 10.3, 7.1 Hz, 1H), 2.08 (d, *J* = 5.0 Hz, 1H), 1.59 – 1.24 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 71.1 (s), 40.8 (s), 35.2, 32.0, 29.6, 29.6, 29.3, 25.7, 22.8, 14.2.

2-Bromodecan-1-ol (3r')

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.16 (dtd, *J* = 10.0, 7.3, 4.2 Hz, 1H **3r'**), 3.94 – 3.58 (m, 2H **3r'** & 1H 3r), 3.55 (dd, *J* = 10.3, 3.2 Hz, 1H 3r), 3.38 (dd, *J* = 10.3, 7.1 Hz, 1H 3r), 2.24 – 1.21 (m, 15H **3r'** & 15H 3r), 0.88 (d, *J* = 13.0 Hz, 3H **3r'** & 3H 2r).

2-Bromocyclohexan-1-ol (3s)



The product was obtained from cyclohexene (0.7 mmol) as a yellow oil (43%, 54 mg, 0.30 mmol, dr >20:1) by using method A.

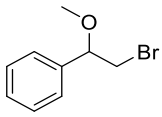
The product was obtained from cyclohexene (1.18 mmol) as a colourless oil (37%, 78 mg, 0.44 mmol) by using method B.

The spectral data are in agreement with the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (ddd, *J* = 12.0, 9.4, 4.4 Hz, 1H), 3.60 (td, *J* = 9.8, 4.8 Hz, 1H), 2.55 (s, 1H), 2.42 – 2.25 (m, 1H), 2.21 – 2.05 (m, 1H), 1.91 – 1.63 (m, 3H), 1.45 – 1.20 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 75.4, 62.0, 36.3, 33.6, 26.8, 24.2.

(2-Bromo-1-methoxyethyl)benzene (4a)

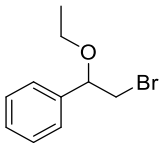


The product was obtained from styrene (100 mM MeOH/MeCN 3:7, 0.7 mmol) as a yellow oil (51%, 77 mg, 0.36 mmol) by using method D. The spectral data are in agreement with the literature.[13]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 5H), 4.39 (dd, *J* = 8.1, 4.4 Hz, 1H), 3.54 (dd, *J* = 10.7, 8.1 Hz, 1H), 3.47 (dd, *J* = 10.7, 4.4 Hz, 1H), 3.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 128.8, 128.7, 126.9, 83.5, 57.4, 36.5.

(2-Bromo-1-ethoxyethyl)benzene (4b)

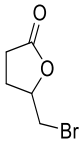


The product was obtained from styrene (100 mM MeOH/MeCN 3:7, 0.7 mmol) as a yellow oil (46%, 74 mg, 0.32 mmol) by using method D. The spectral data are in agreement with the literature.[13]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 5H), 4.49 (dd, *J* = 8.1, 4.5 Hz, 1H), 3.58 – 3.41 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 128.7, 128.5, 126.8, 81.8, 65.1, 36.7, 15.3.

5-(Bromomethyl)dihydrofuran-2(3H)-one (4c)

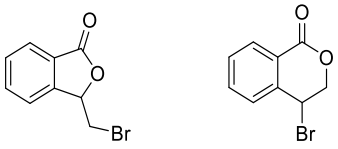


The product was obtained from 4-pentenoic acid (100mM in 100 % MeCN, 0.34 mmol) as a paleyellow oil (74%, 44 mg, 0.25 mmol) by using modified method A. The spectral data are in agreement with the literature.[14] (Armstrong et al., Tetrahedron Letters, 2013, 7004)

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.75 (dtd, *J* = 10.8, 6.2, 4.4 Hz, 1H), 3.61 – 3.48 (m, 2H), 2.73 – 2.52 (m, 2H), 2.51 – 2.38 (m, 1H), 2.19 – 2.06 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 77.9, 34.2, 28.5, 26.3.

3-(Bromomethyl)isobenzofuran-1(3H)-one (4d) & 4-bromoisochroman-1-one (4d')



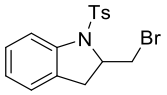
4d **4d'**

The product was obtained from 2-vinylbenzoic acid (0.7 mmol) as an off-white solid (57%, 90 mg, 0.40 mmol, mixture of regioisomers **4d**/**4d'** 9:1) by using method B. The spectral data are in agreement with the literature.[14,15]

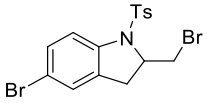
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 1H **4d'**), 7.92 (d, *J* = 7.6 Hz, 1H **4d**), 7.77 – 7.67 (m, 1H **4d**), 7.67 – 7.55 (m, 2H **4d** & 1H **4d'**), 7.52 (dd, *J* = 7.6, 1.1 Hz, 1H **4d'**), 7.47 (d, *J* = 7.7 Hz, 1H **4d'**), 5.70 (t, *J* = 5.0 Hz, 1H **4d**), 5.34 (t, *J* = 2.9 Hz, 1H **4d'**), 4.78 (dd, *J* = 12.7, 2.8 Hz, 1H **4d'**), 4.71 (dd, *J* = 12.7, 3.1 Hz, 1H **4d'**), 3.77 (d, *J* = 5.0 Hz, 2H **4d**).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5 (**4d**), 147.2 (**4d**), 139.5 (**4d'**), 134.5 (**4d'**), 134.4 (**4d**), 130.8 (**4d'**), 130.1 (**4d** & **4d'**), 127.4 (**4d'**), 126.4 (**4d**), 125.9 (**4d**), 123.9 (**4d'**), 122.5 (**4d**), 78.7 (**4d**), 72.1 (**4d'**), 41.3 (**4d'**), 32.4 (**4d**).

2-(Bromomethyl)-1-tosylindoline (4e) & 5-bromo-2-(bromomethyl)-1-tosylindoline (4e')



4e



4e'

The products were obtained from N-(2-allylphenyl)-4-methylbenzenesulfonamide (100mM in H_2O/MeCN 5:95, 0.76 mmol) as white solids (22%, 62 mg, 0.17 mmol, **4e** & 21%, 70 mg, 0.16 mmol, **4e'**) by using a modified method A. The separation of mono and dibrominated products by column chromatography afforded pure 2-(bromomethyl)-1-tosylindoline (30 mg, **4e**), a mixture of 2-(bromomethyl)-1-tosylindoline and 5-bromo-2-(bromomethyl)-1-tosylindoline (72 mg, **4e**/**4e'** 1.00:1.04) and pure 5-bromo-2-(bromomethyl)-1-tosylindoline (30 mg, **4e'**). The spectral data are in agreement with the literature.[16]

2-(Bromomethyl)-1-tosylindoline (4e)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 – 6.99 (m, 2H), 4.43 (dddd, *J* = 9.9, 7.4, 5.2, 3.8 Hz, 1H), 3.82 (dd, *J* = 9.9, 3.7 Hz, 1H), 3.41 (t, *J* = 9.9 Hz, 1H), 2.98 – 2.83 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 141.2, 134.5, 130.7, 129.9, 128.1, 127.2, 125.4, 125.1, 117.0, 62.3, 36.1, 33.3, 21.7.

HRMS (EI+) *m/z*: calcd. for $[M]^+$ ($C_{16}H_{16}O_2N^{79}Br^{32}S$): 365.00796; found: 365.0076.

MP: 154-156 °C.

5-Bromo-2-(bromomethyl)-1-tosylindoline (4e')

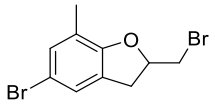
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.34 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 1.6 Hz, 1H), 4.42 (dddd, *J* = 9.3, 7.4, 5.4, 3.7 Hz, 1H), 3.79 (dd, *J* = 10.0, 3.7 Hz, 1H), 3.42 (t, *J* = 9.8 Hz, 1H), 2.91 (d, *J* = 6.1 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 140.6, 134.2, 133.0, 131.1, 130.1, 128.5, 127.2, 118.2, 117.9, 62.4, 36.0, 33.1, 21.7.

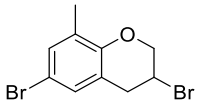
HRMS (EI+) *m/z*: calcd. for $[M]^+$ ($C_{16}H_{16}O_2N^{79}Br^{81}Br^{32}S$): 444.91643; found: 444.9161.

MP: 120-122 °C.

5-Bromo-2-(bromomethyl)-7-methyl-2,3-dihydrobenzofuran (4f) & 3,6-dibromo-8-methylchromane (4f')



4f



4f'

The product was obtained from 2-allyl-6-methylphenol (100 mM in 100% MeCN, 0.74 mmol) as a colourless oil (22%, 50 mg, 0.40 mmol, mixture of regioisomers **4f**/**4f'** 2.33:1) by using a modified method A. The ratio of regioisomers in the isolated product mixture does not reflect selectivity. The spectral data are in agreement with the literature.[17]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (s, 1H **4f'**), 7.14 (s, 1H **4f'**), 7.10 (s, 1H **4f**), 7.07 (s, 1H **4f**), 5.05 – 4.94 (m, 1H **4f**), 4.66 (t, *J* = 9.1 Hz, 1H **4f'**), 4.47 (dd, *J* = 9.5, 5.4 Hz, 1H **4f'**), 3.91 – 3.80 (m, 1H, **4f'**), 3.63 – 3.55 (m, 1H **4f** & 1H **4f'**), 3.49 (dd, *J* = 10.4, 7.1 Hz, 1H **4f**), 3.43 – 3.32 (m, 1H **4f** & 1H **4f'**), 3.12 (dd, *J* = 16.1, 6.5 Hz, 1H **4f**), 2.17 & 2.18 (s, 3H **4f** & s 3H **4f'**).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0 (**4f'**), 156.9 (**4f**), 133.3 (**4f'**), 132.1 (**4f**), 129.0 (**4f'**), 127.2 (**4f**), 125.3 (**4f**), 125.0 (**4f'**), 122.5 (**4f'**), 121.8 (**4f**), 112.5 (**4f**), 112.2 (**4f'**), 81.3 (**4f**), 76.2 (**4f'**), 45.0 (**4f'**), 34.7 (**4f**), 34.7 (**4f'**), 34.5 (**4f**), 15.2 (**4f**), 15.1 (**4f'**).

HRMS (CI+) *m/z*: calcd. $[M]^+$ ($C_{10}H_{10}O^{79}Br_2$): 303.90929; found: 303.9097.

The reaction of 4-pentenol and 5-hexenol under modified conditions A without cosolvent did not lead to the formation of cyclized products.

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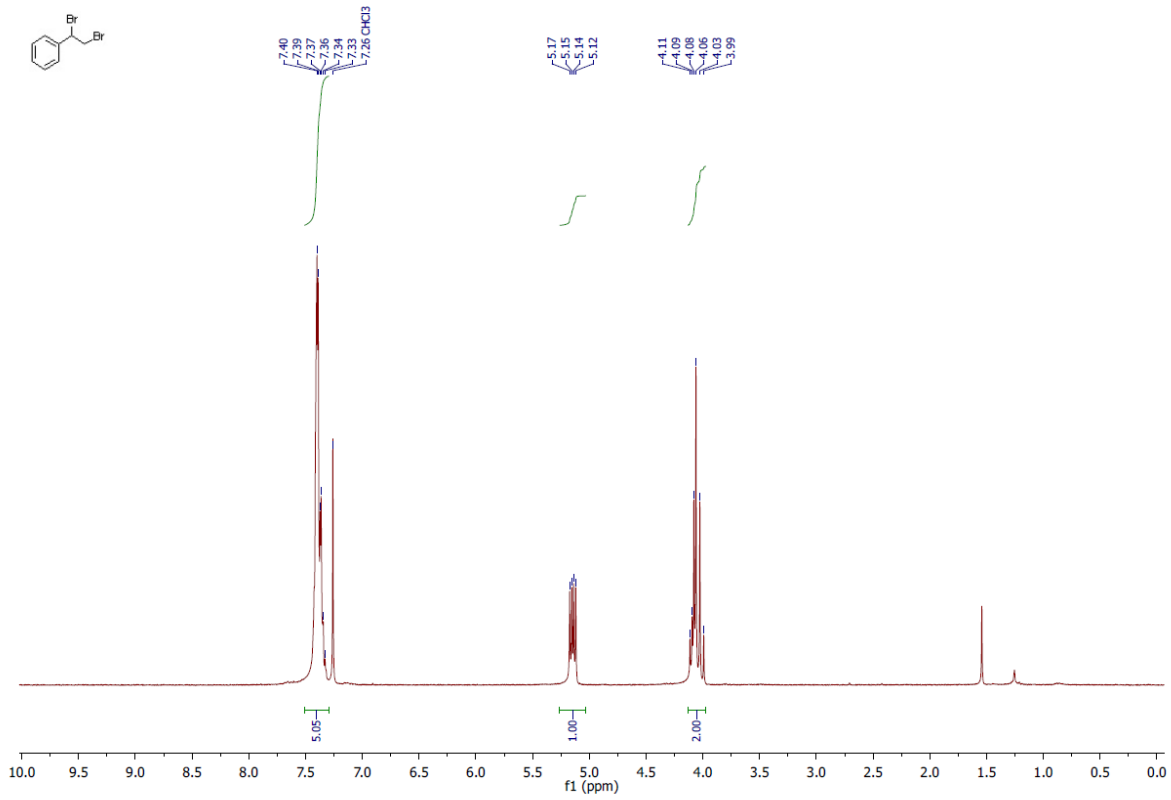
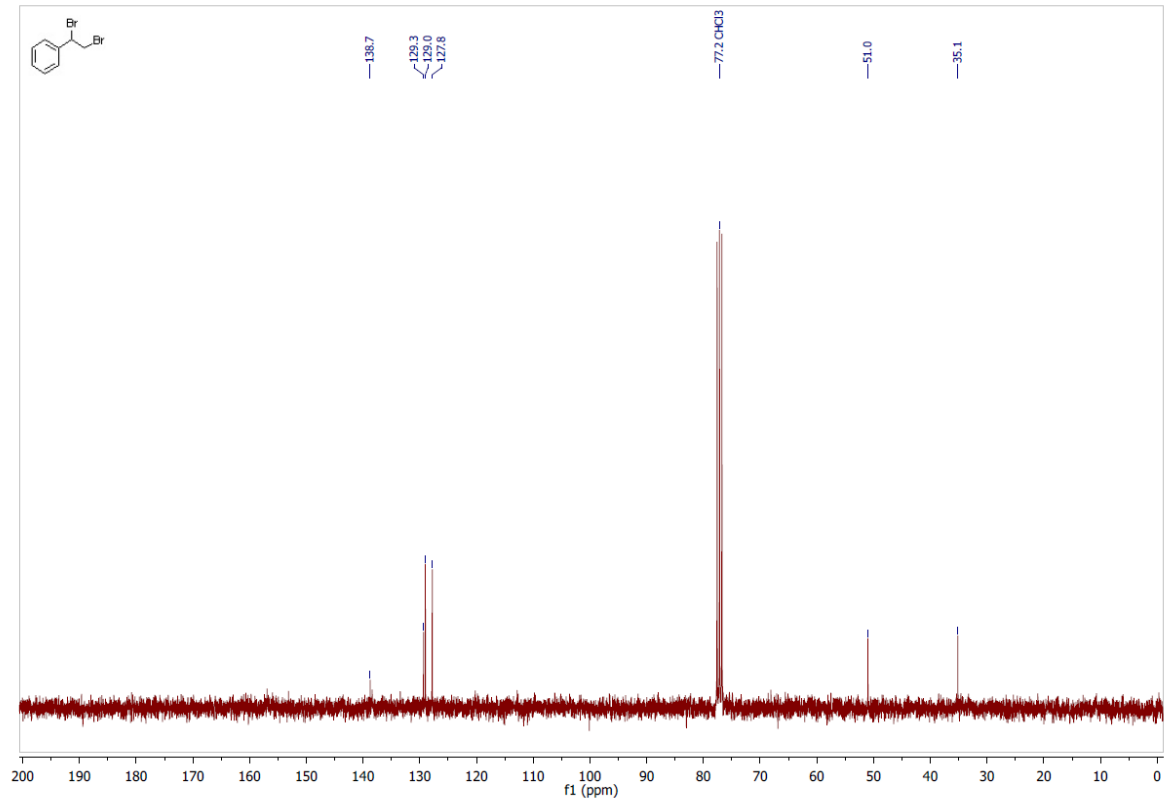
NMR Spectra

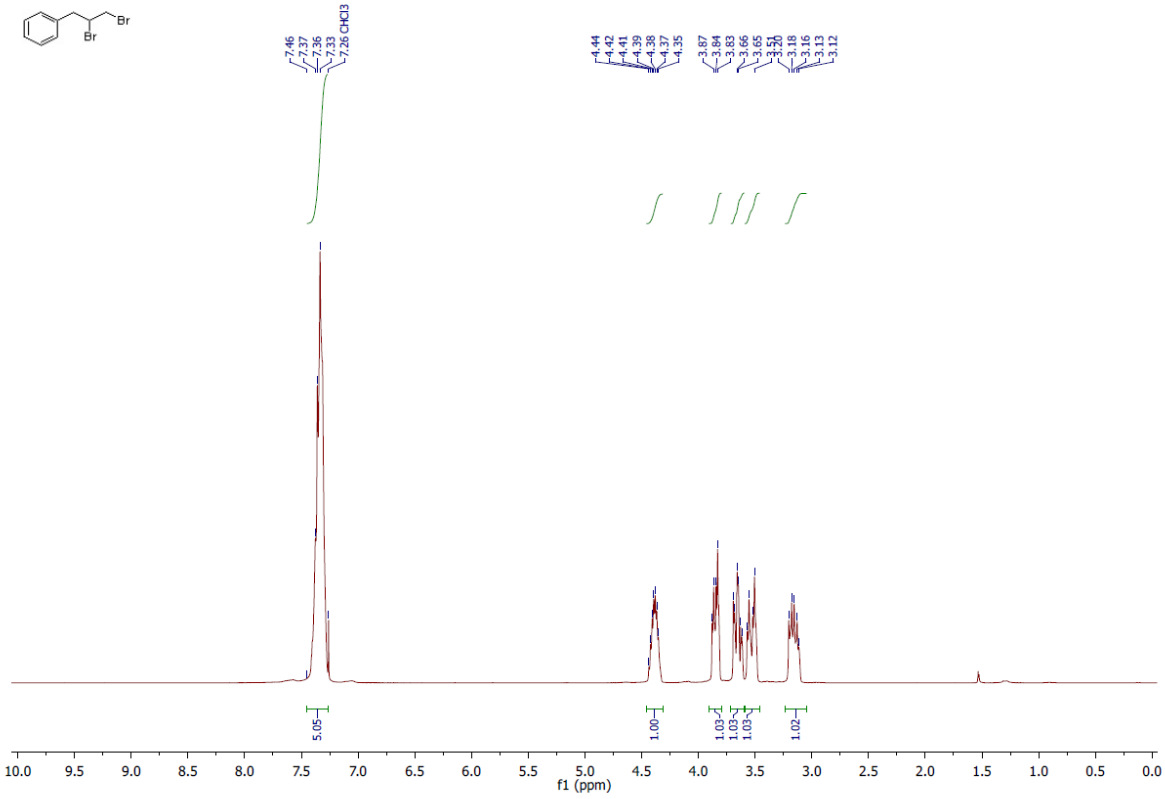
^{1}H NMR (300 MHz, $CDCl_3$) of (1,2-dibromoethyl)benzene (**2a**)



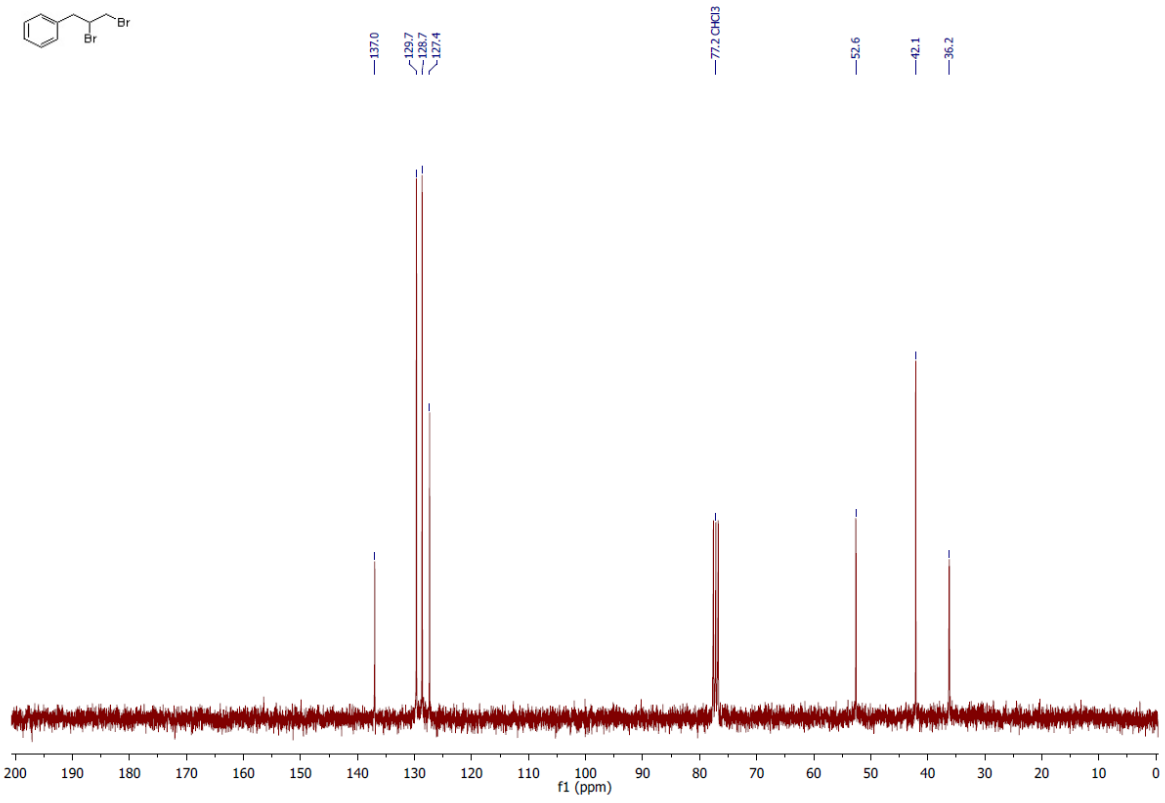
^{13}C NMR (75 MHz, $CDCl_3$) of (1,2-dibromoethyl)benzene (**2a**)



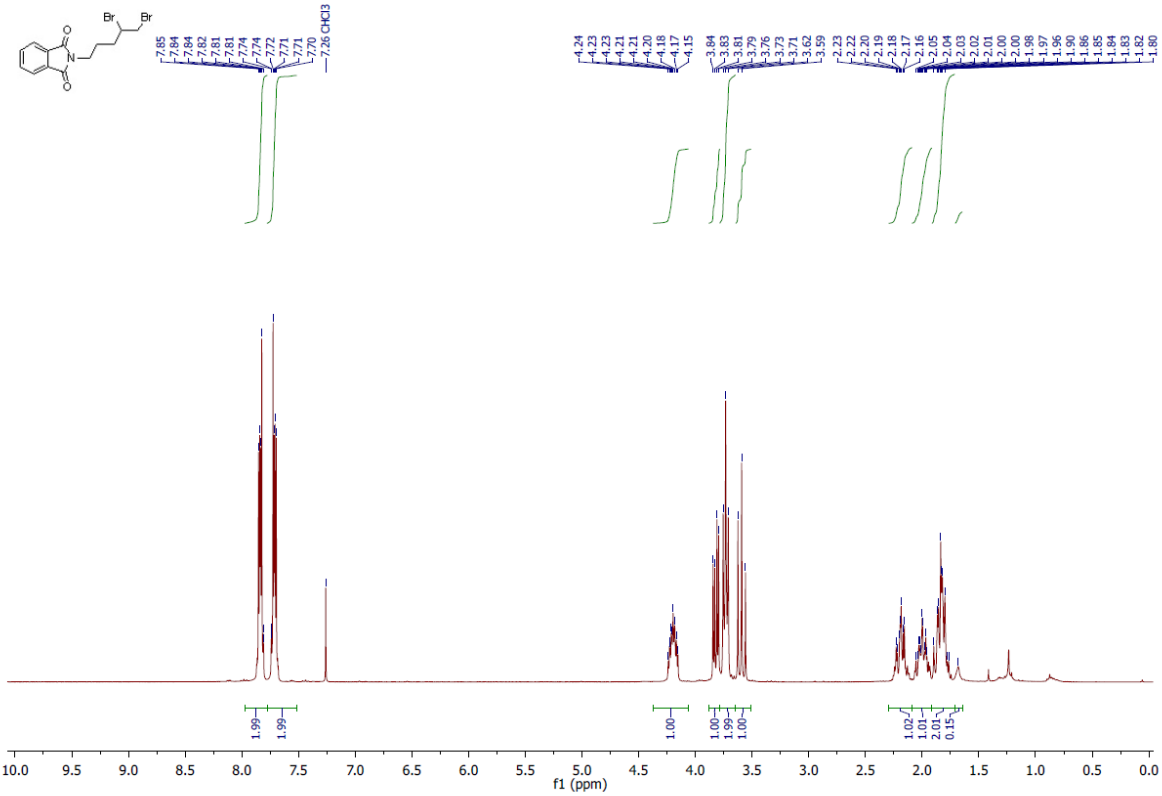
^{1}H NMR (300 MHz, $CDCl_3$) of (2,3-dibromopropyl)benzene (**2b**)



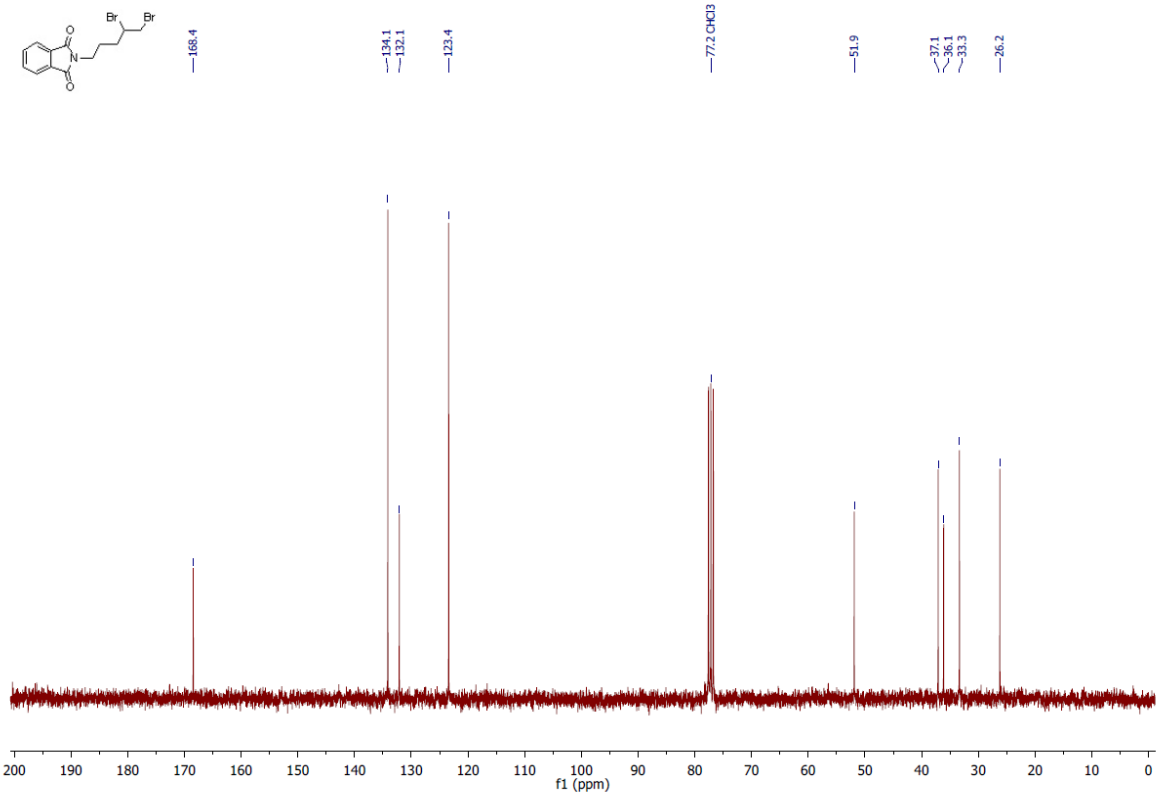
^{13}C NMR (75 MHz, $CDCl_3$) of (2,3-dibromopropyl)benzene (**2b**)



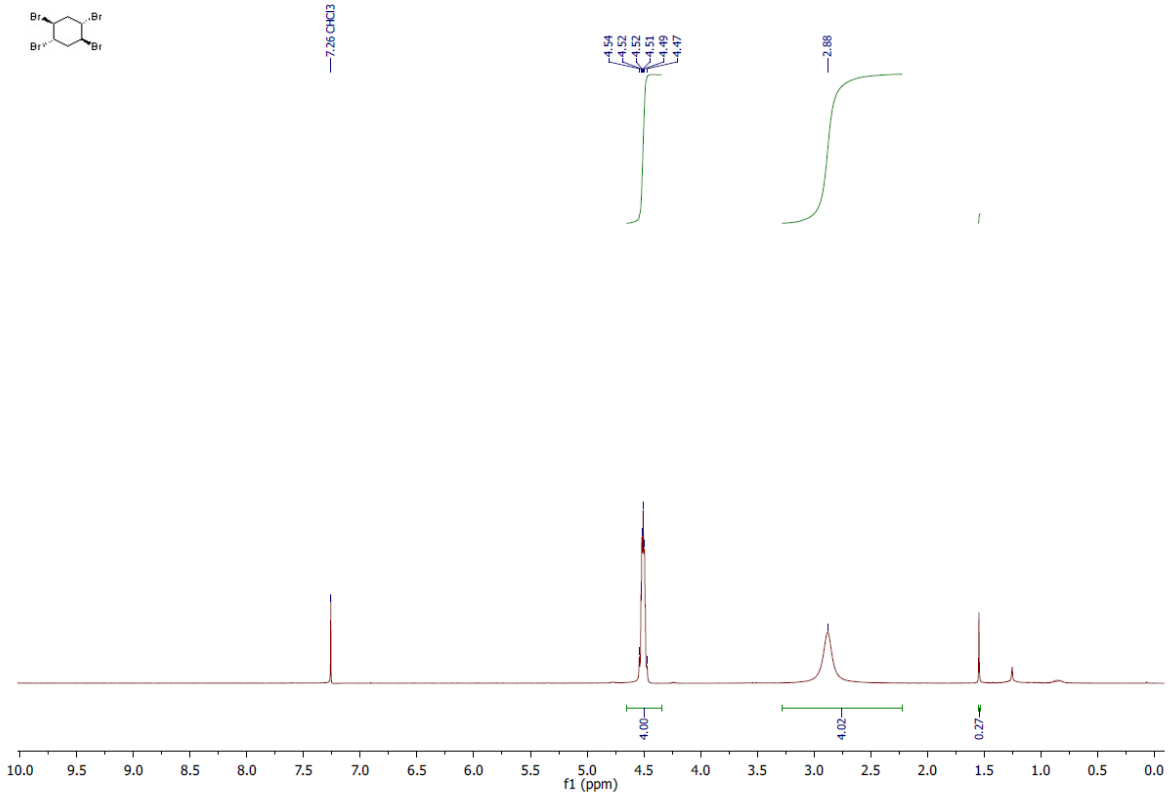
^{1}H NMR (300 MHz, $CDCl_3$) for 2-(4,5-dibromopentyl)isoindoline-1,3-dione (**2c**)



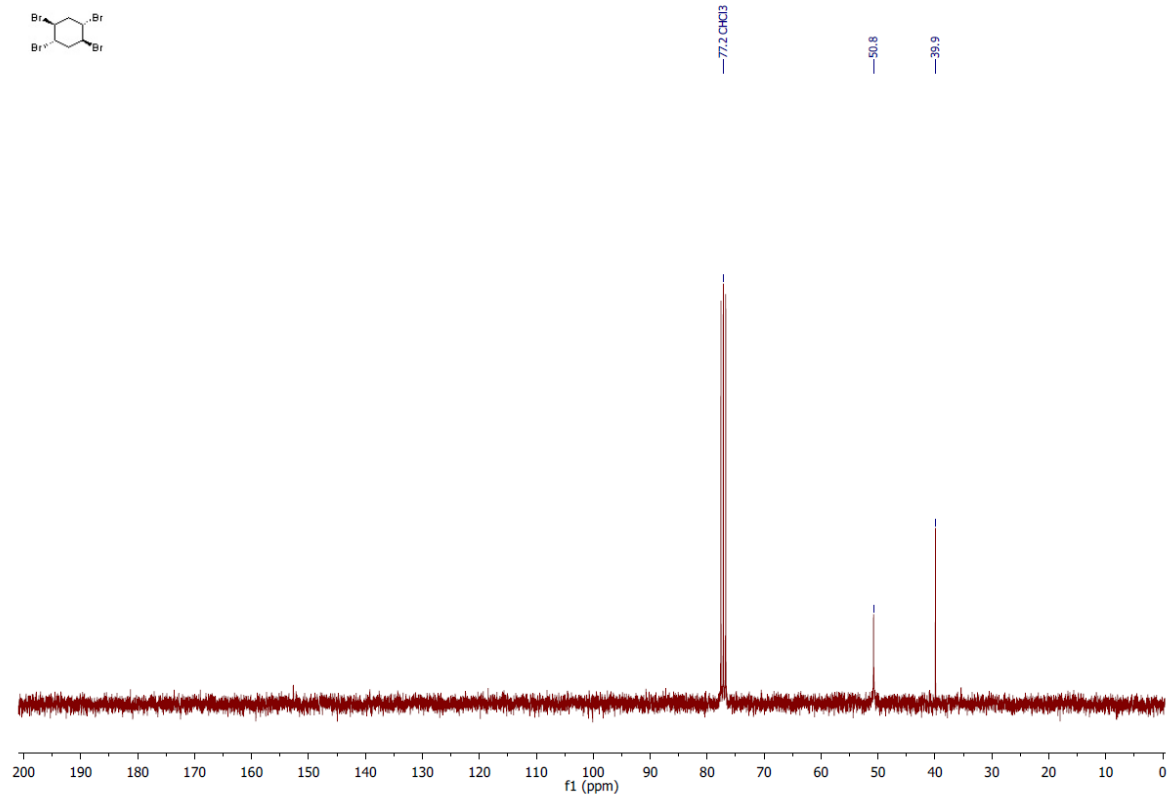
^{13}C NMR (75 MHz, $CDCl_3$) for 2-(4,5-dibromopentyl)isoindoline-1,3-dione (**2c**)



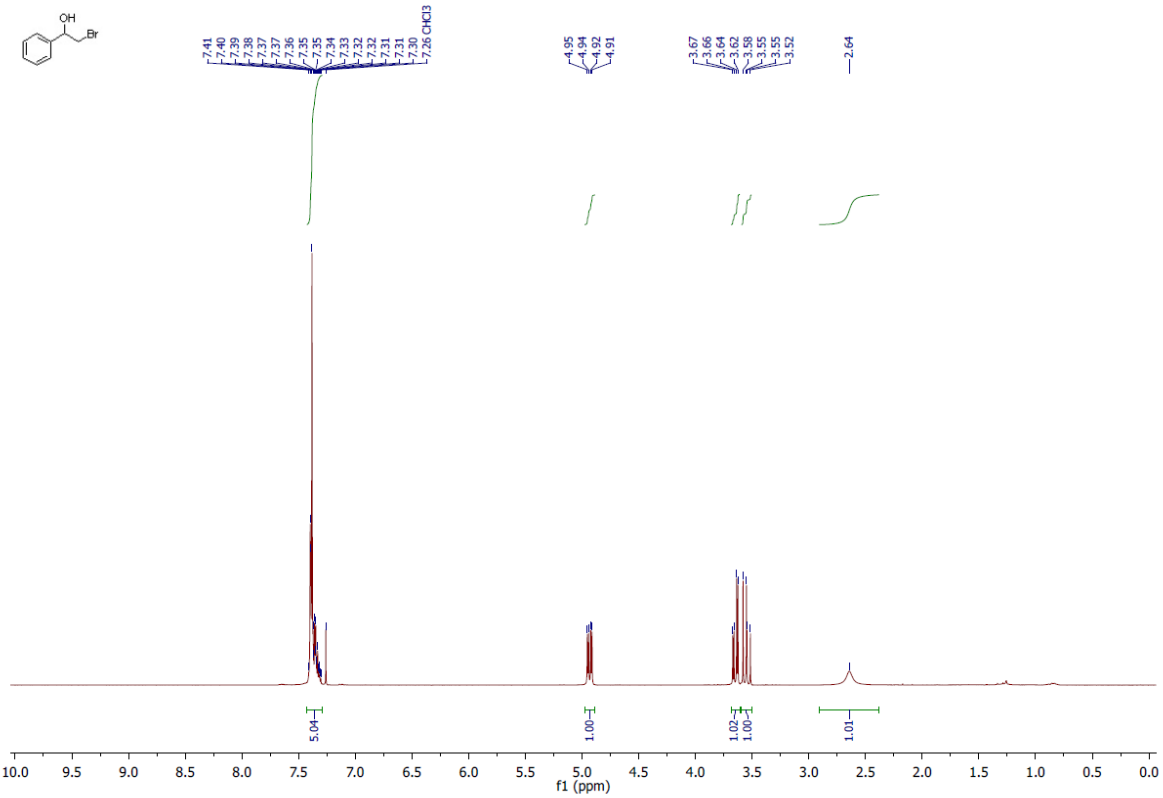
^{1}H NMR (300 MHz, $CDCl_3$) of (1S,2S,4S,5S)-1,2,4,5-tetrabromocyclohexane (**2d**)



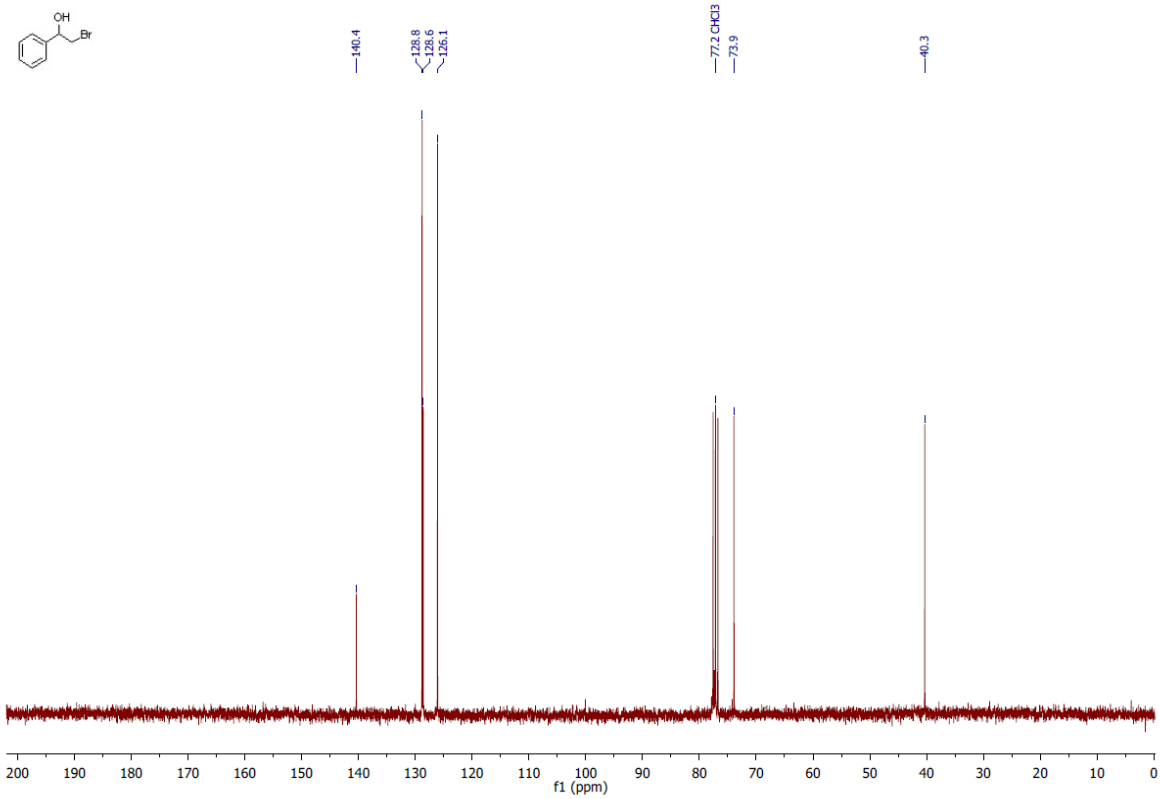
^{13}C NMR (75 MHz, $CDCl_3$) of (1S,2S,4S,5S)-1,2,4,5-tetrabromocyclohexane (**2d**)



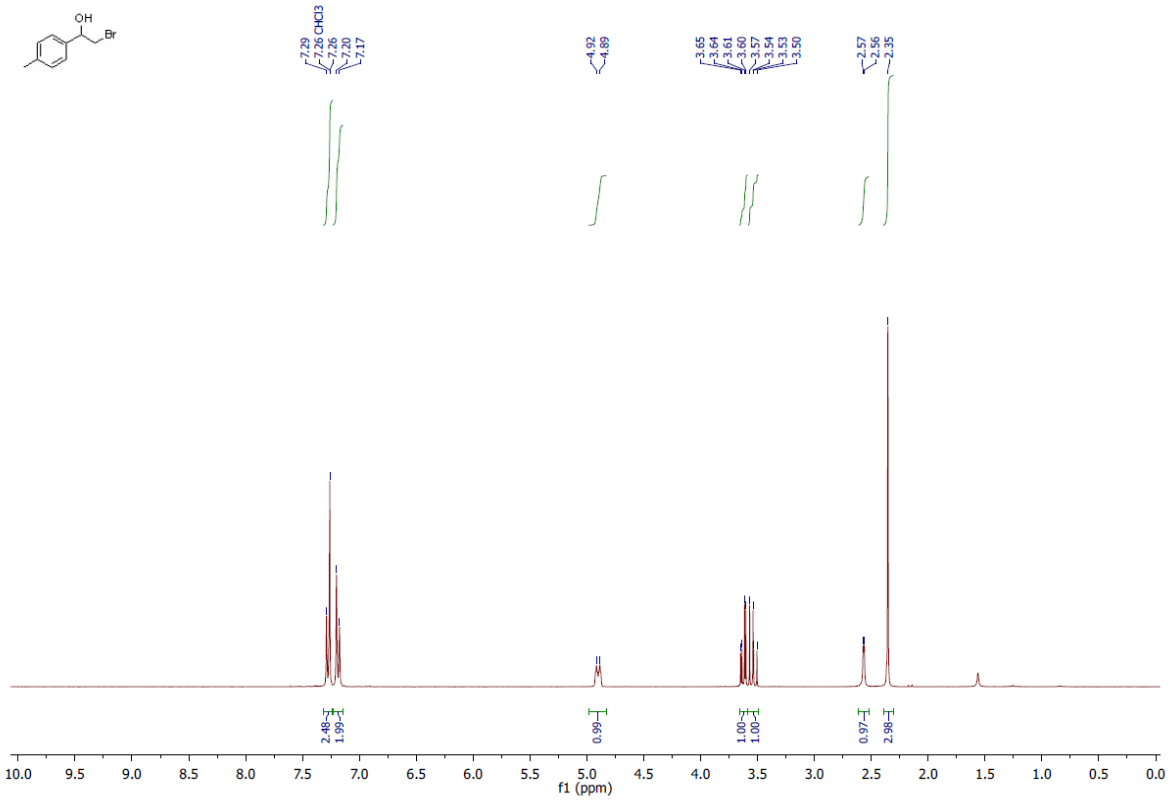
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-1-phenylethan-1-ol (**3a**)



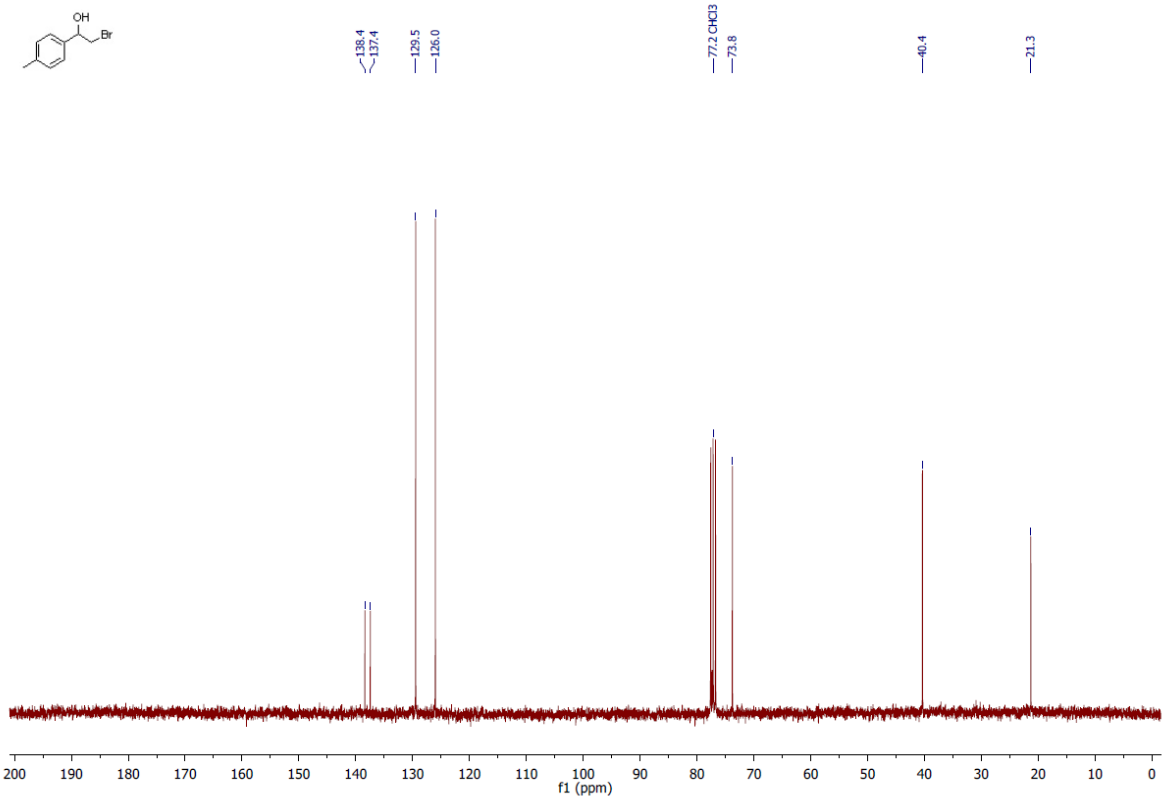
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-1-phenylethan-1-ol (**3a**)



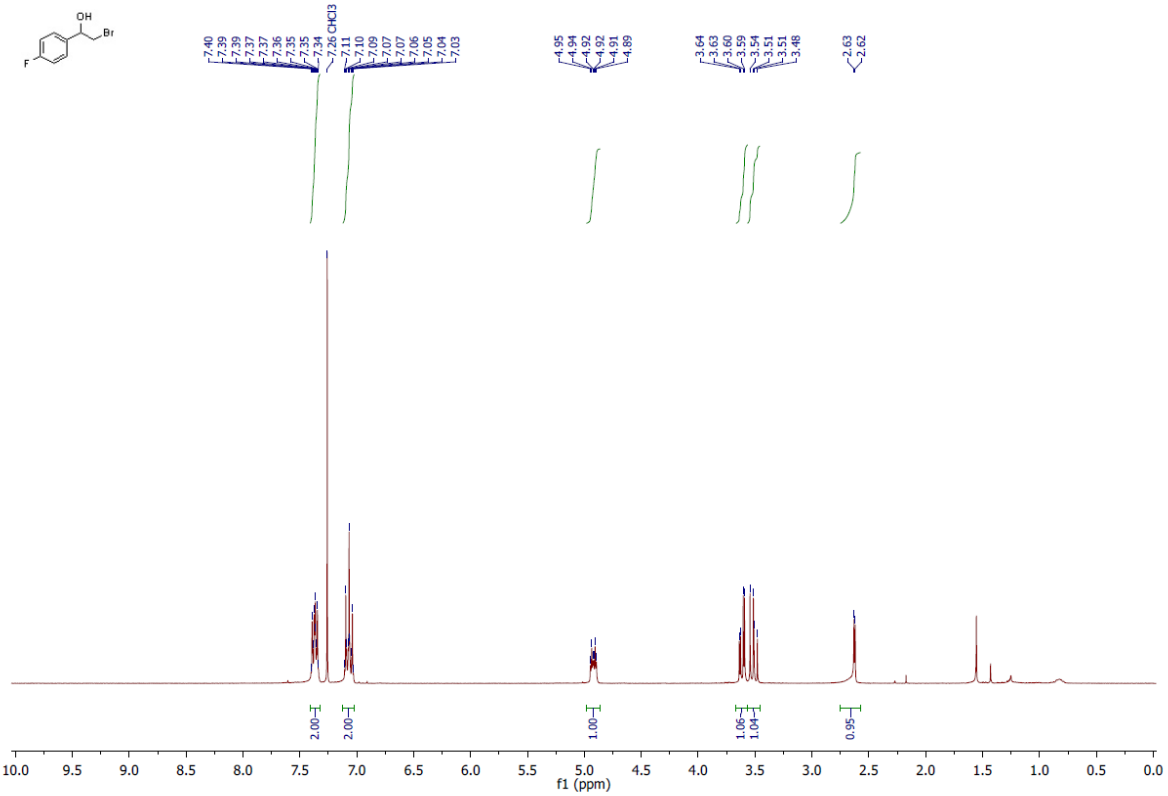
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-1-(p-tolyl)ethan-1-ol (**3b**)



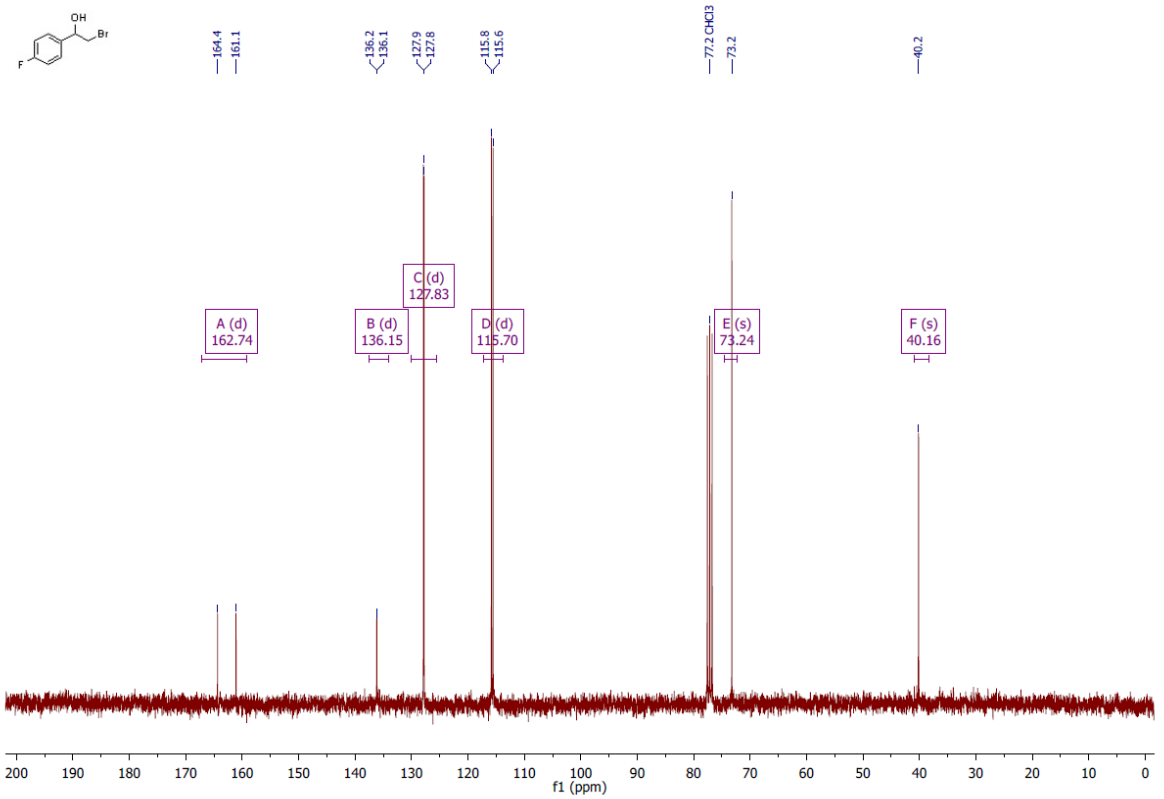
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-1-(p-tolyl)ethan-1-ol (**3b**)



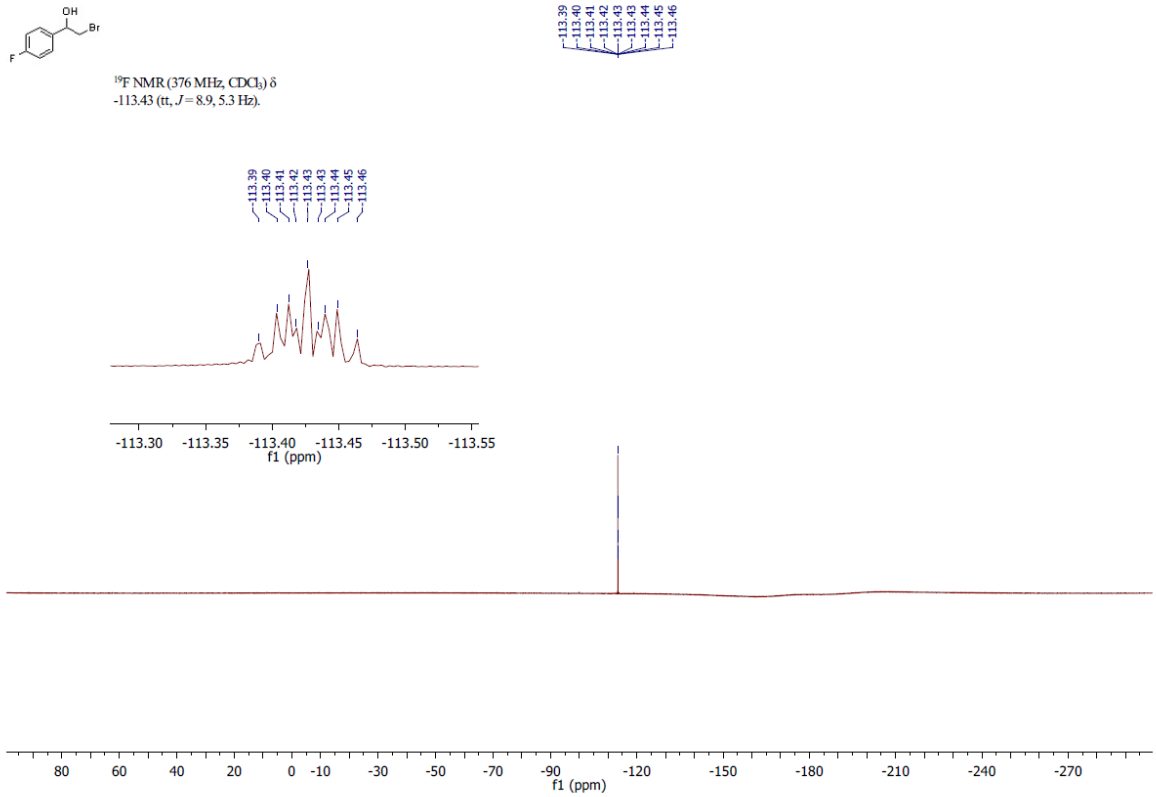
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-1-(4-fluorophenyl)ethan-1-ol (**3c**)



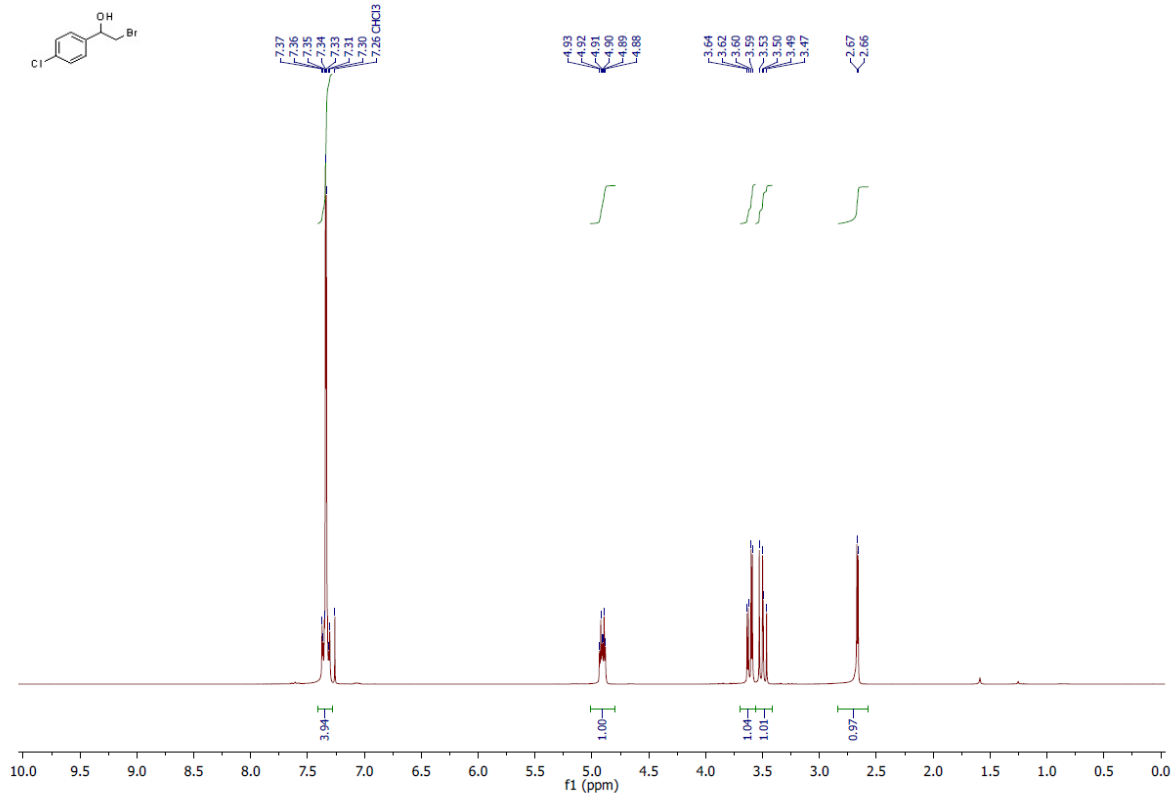
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-1-(4-fluorophenyl)ethan-1-ol (**3c**)



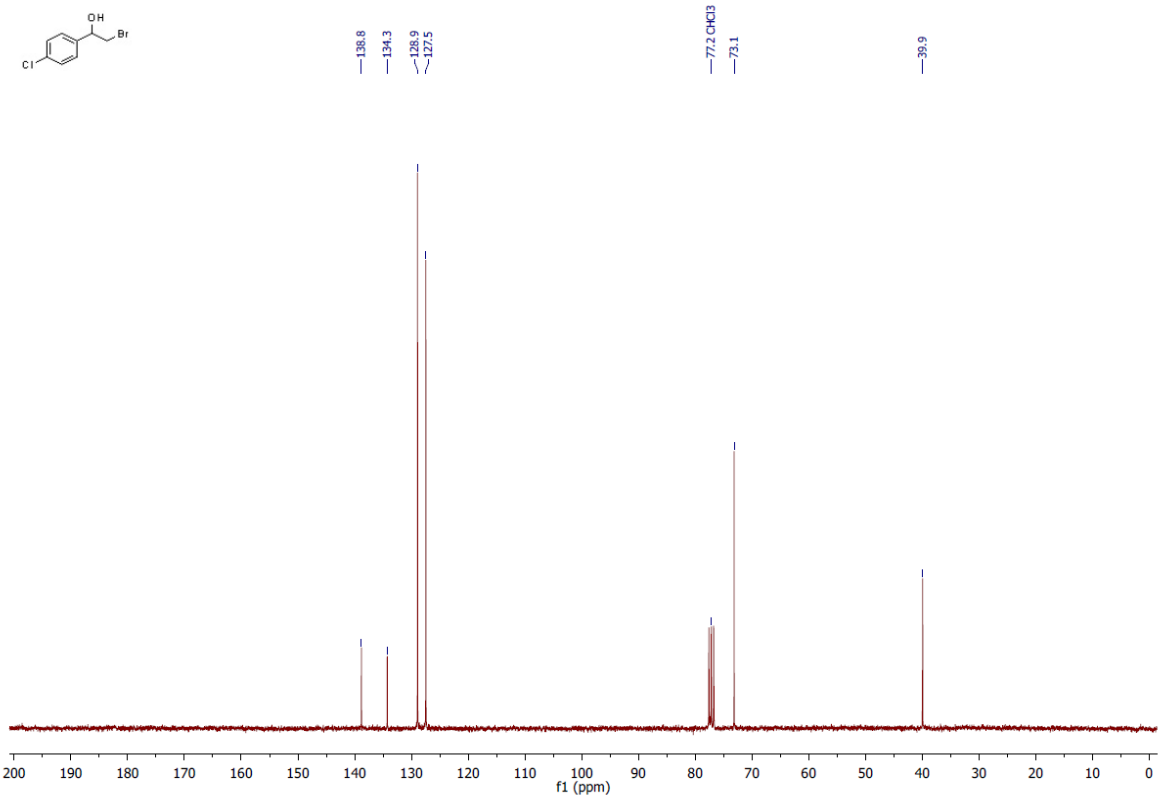
^{19}F NMR of 2-bromo-1-(4-fluorophenyl)ethan-1-ol (**3c**)



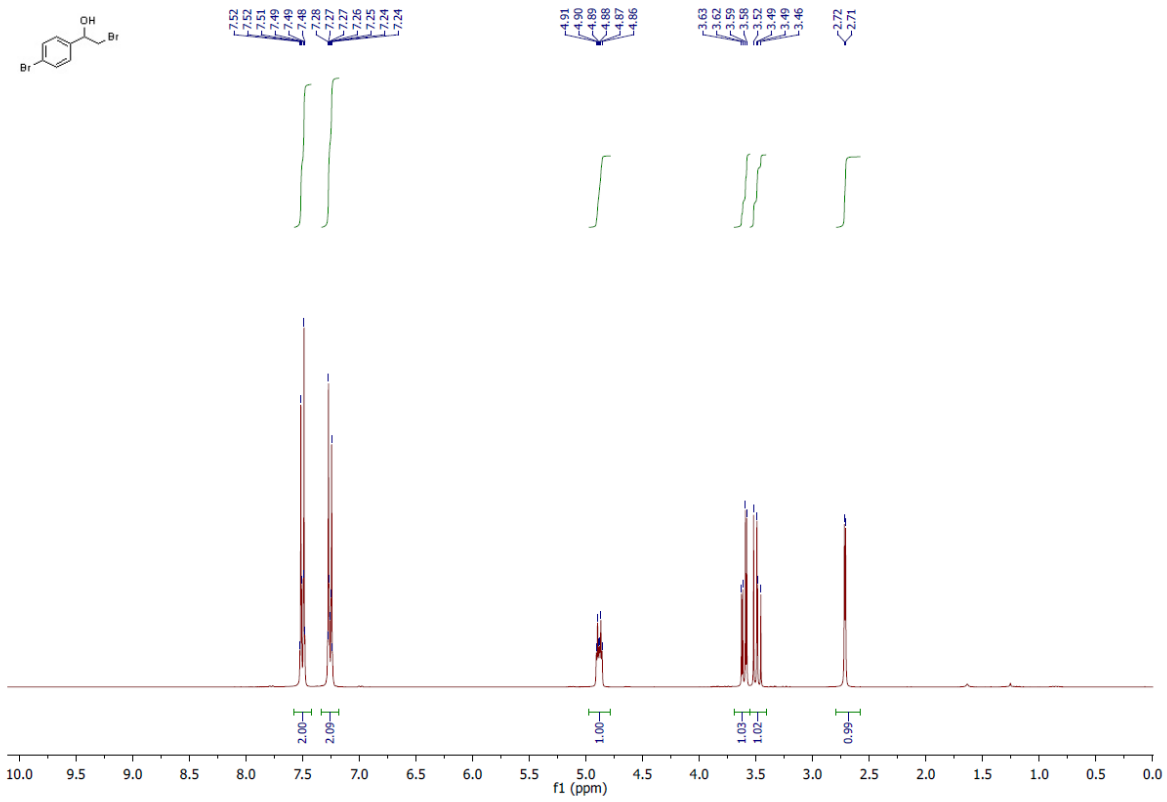
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-1-(4-chlorophenyl)ethan-1-ol (**3d**)



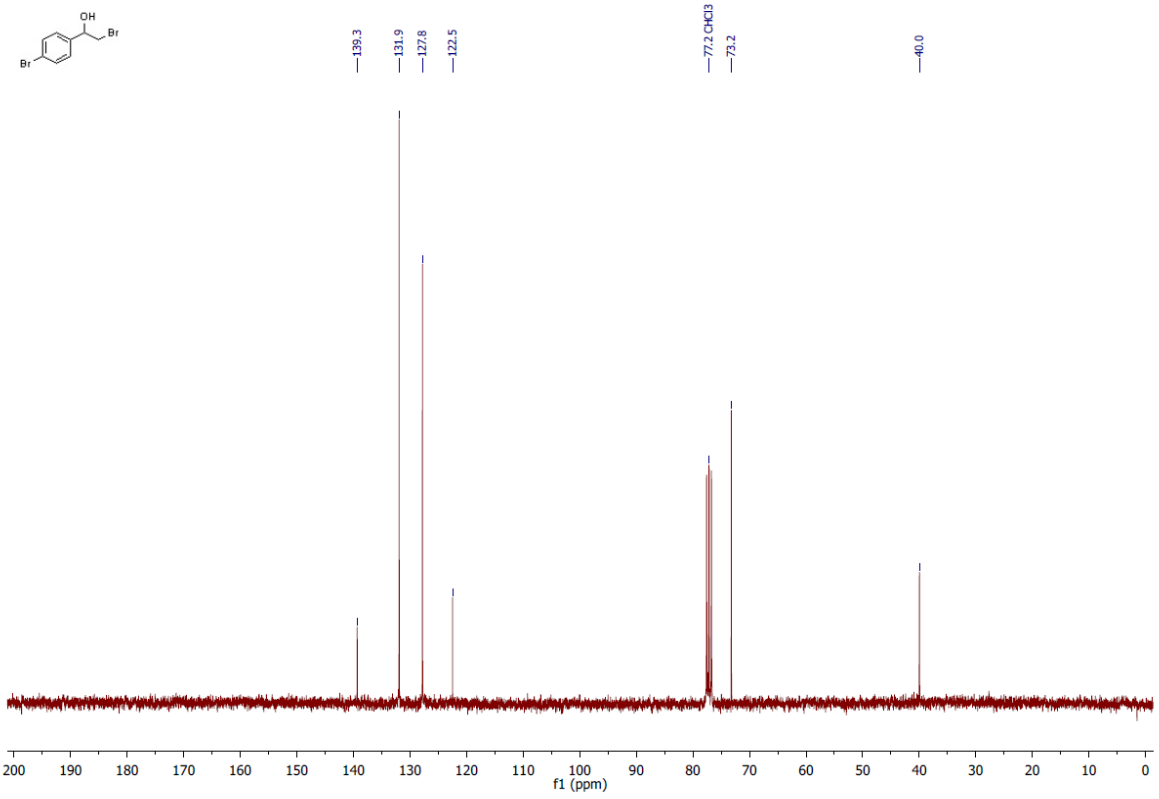
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-1-(4-chlorophenyl)ethan-1-ol (**3d**)



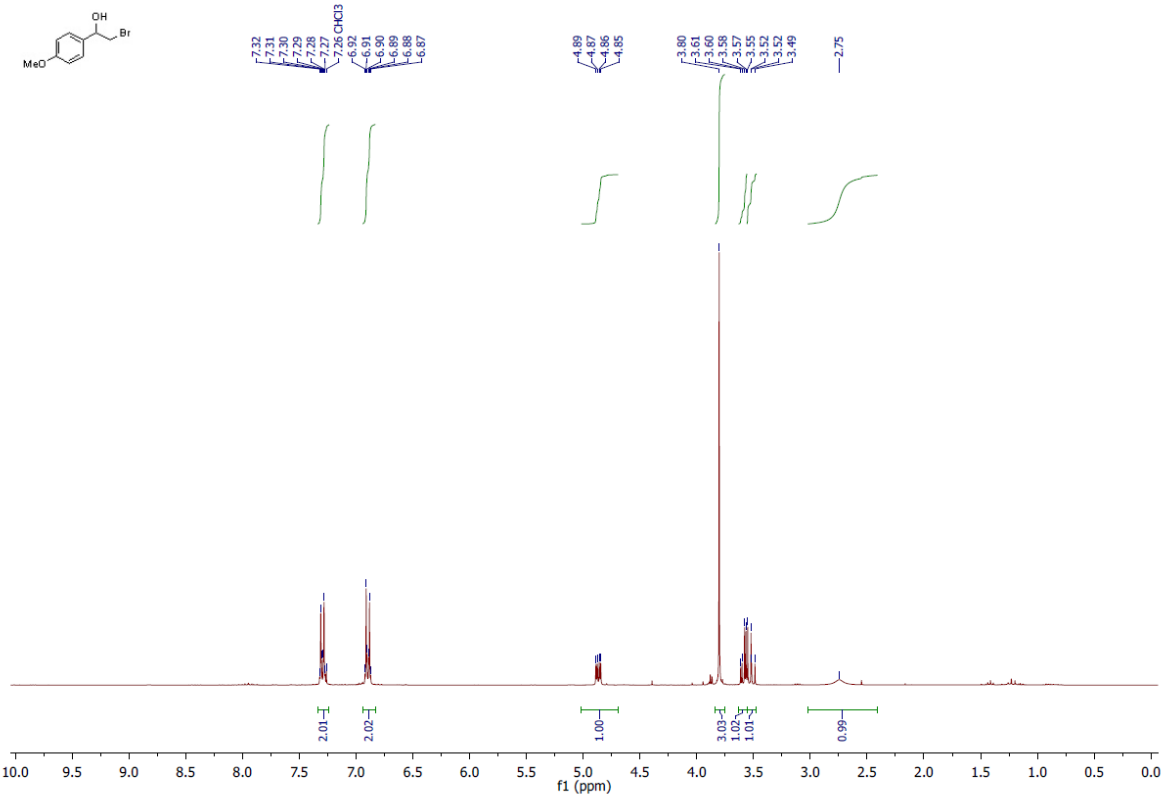
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-1-(4-bromophenyl)ethan-1-ol (**3e**)



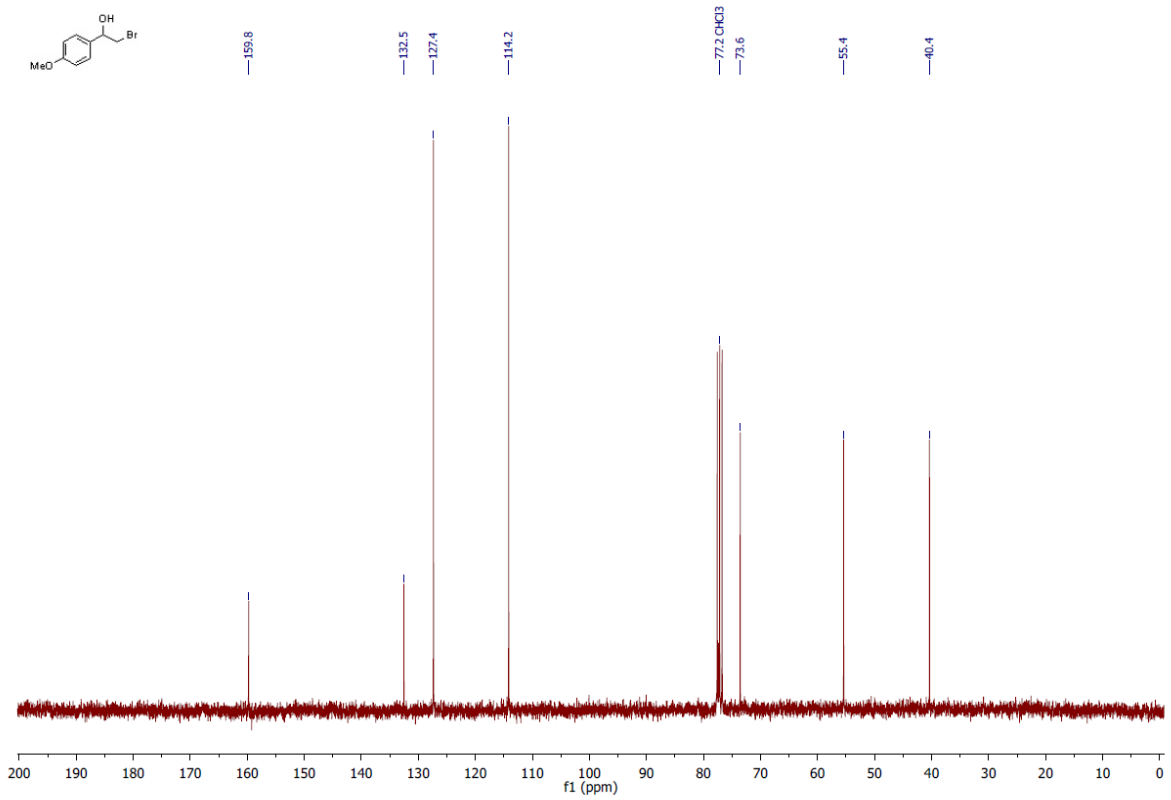
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-1-(4-bromophenyl)ethan-1-ol (**3e**)



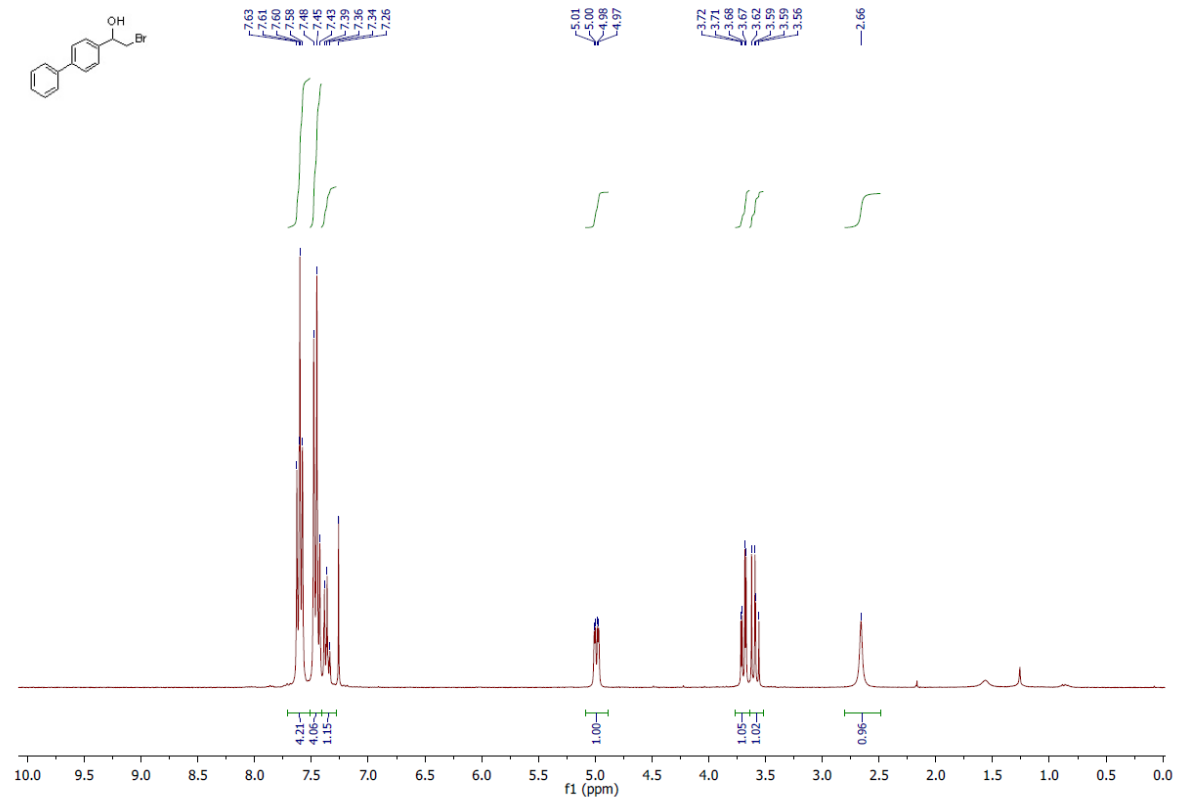
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-1-(4-methoxyphenyl)ethan-1-ol (**3f**)



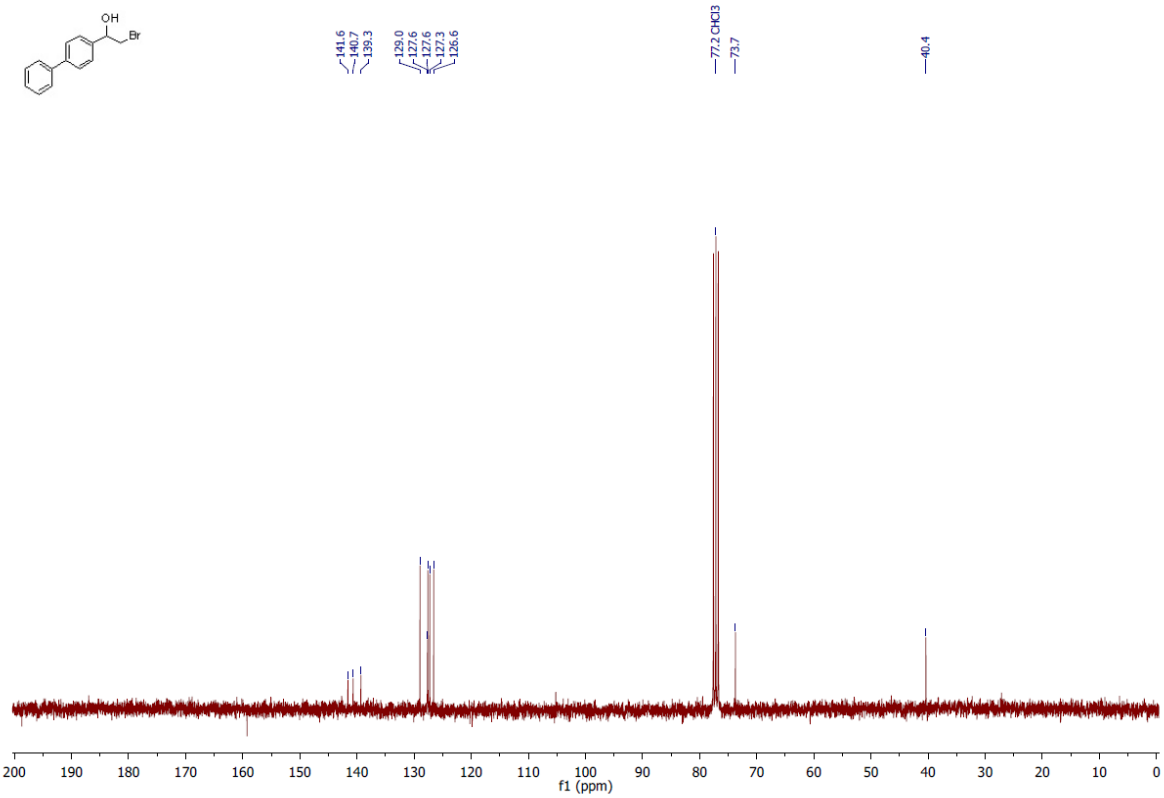
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-1-(4-methoxyphenyl)ethan-1-ol (**3f**)



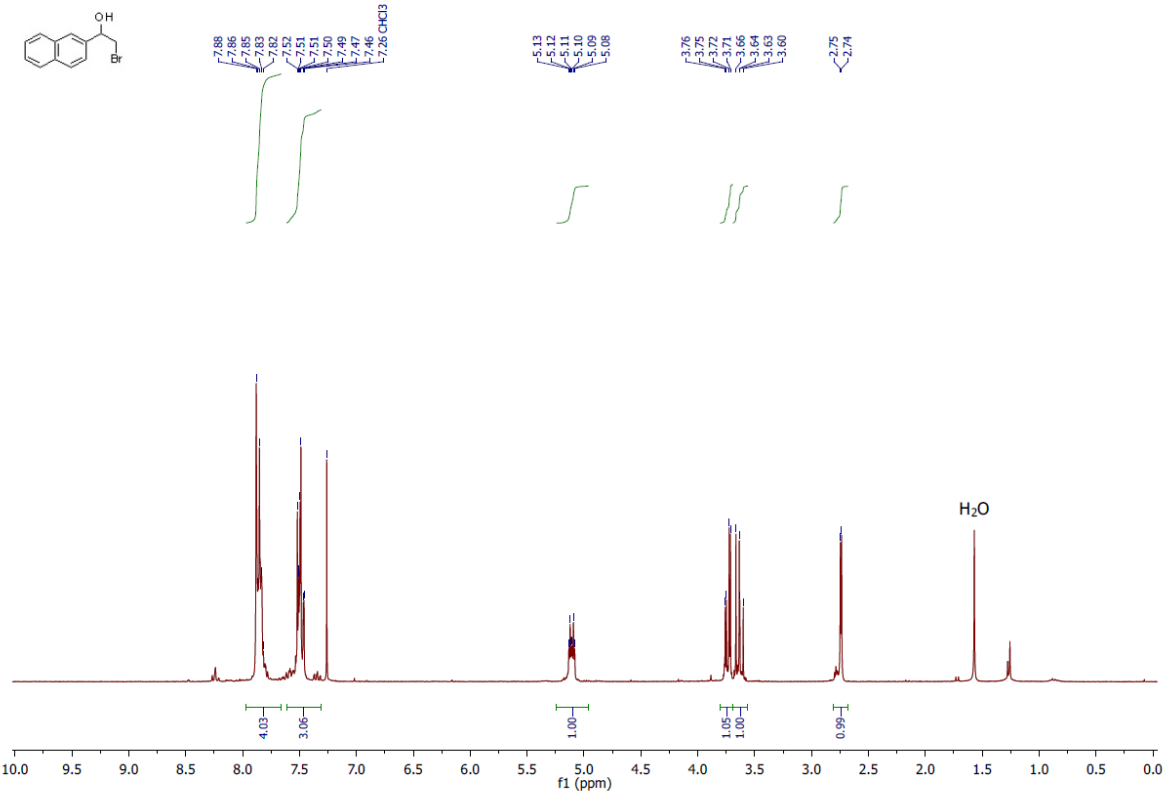
^{1}H NMR (300 MHz, $CDCl_3$) of 1-([1,1'-biphenyl]-4-yl)-2-bromoethan-1-ol (**3g**)



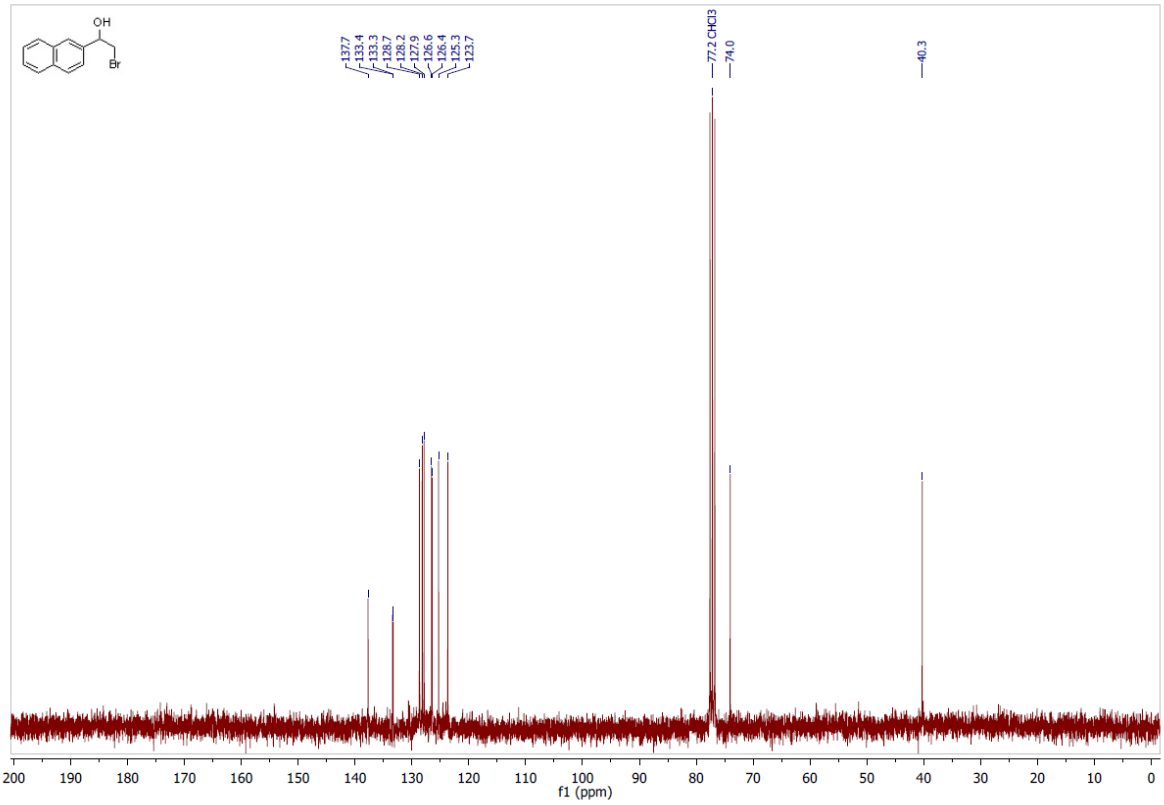
^{13}C NMR (75 MHz, $CDCl_3$) of 1-([1,1'-biphenyl]-4-yl)-2-bromoethan-1-ol (**3g**)



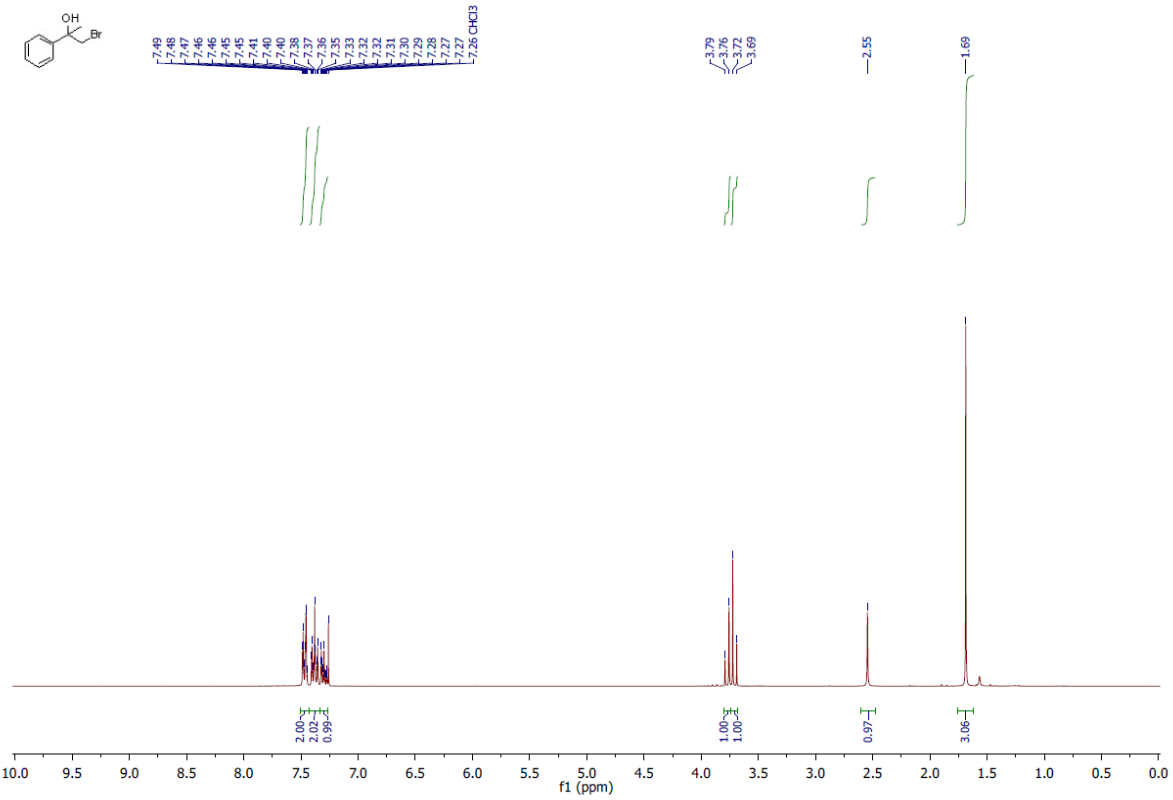
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-1-(naphthalen-2-yl)ethan-1-ol (**3h**)



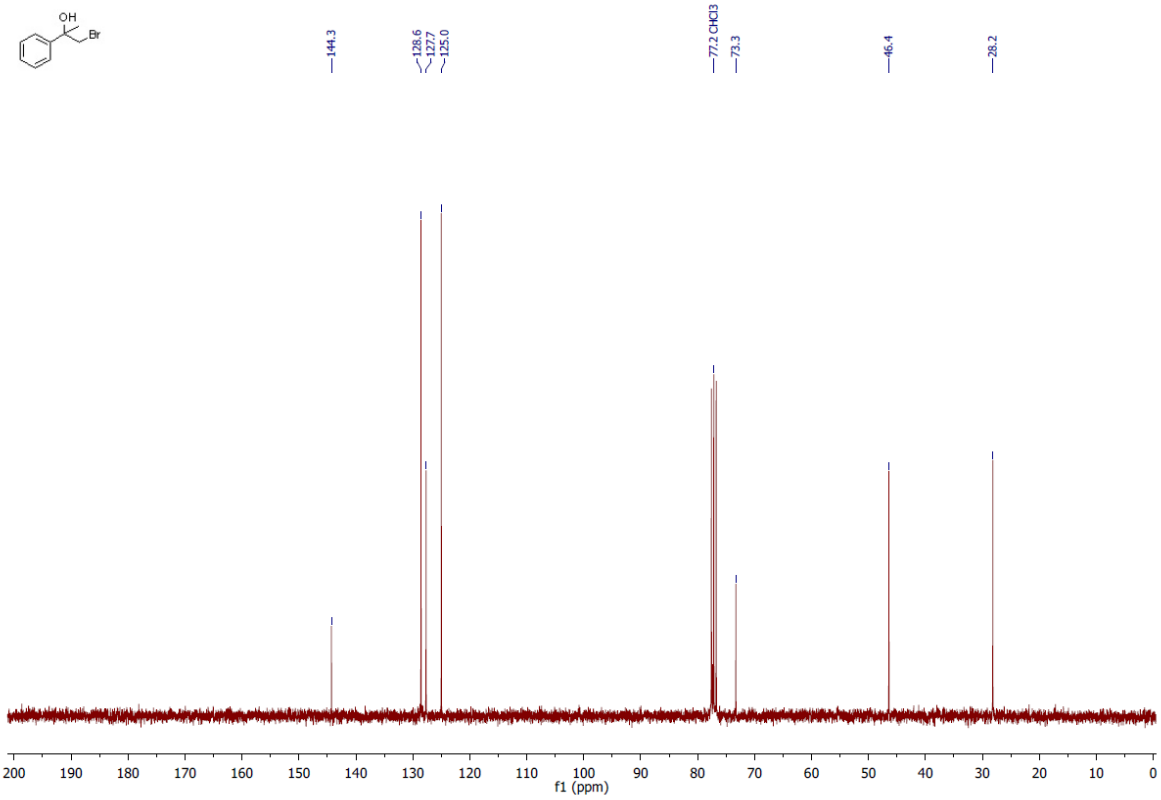
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-1-(naphthalen-2-yl)ethan-1-ol (**3h**)



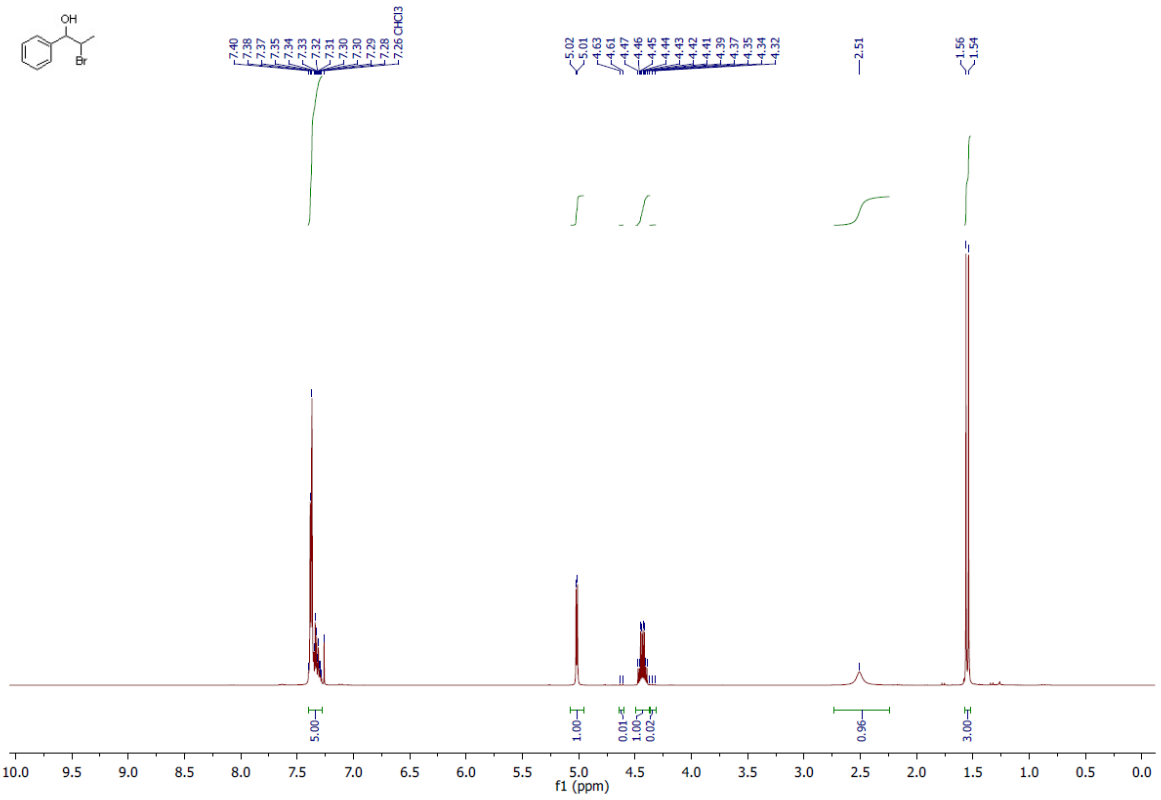
^{1}H NMR (300 MHz, $CDCl_3$) of 1-bromo-2-phenylpropan-2-ol (**3i**)



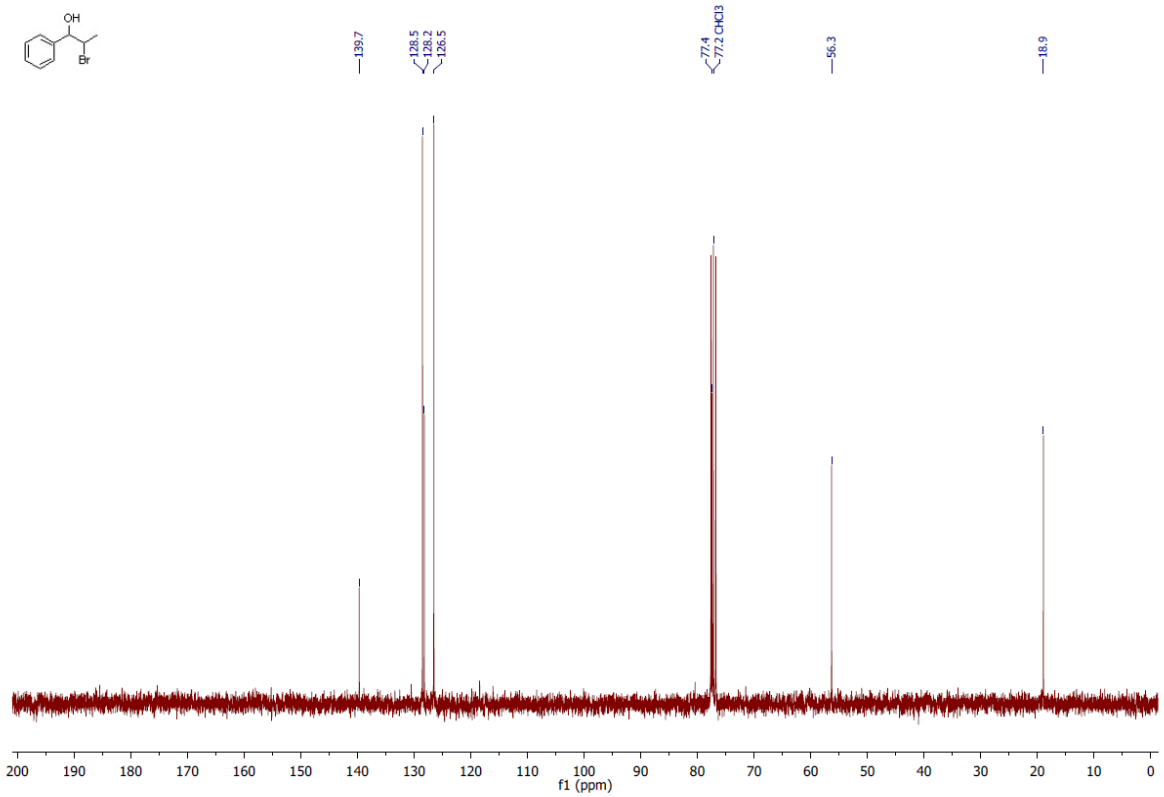
^{13}C NMR (75 MHz, $CDCl_3$) of 1-bromo-2-phenylpropan-2-ol (**3i**)



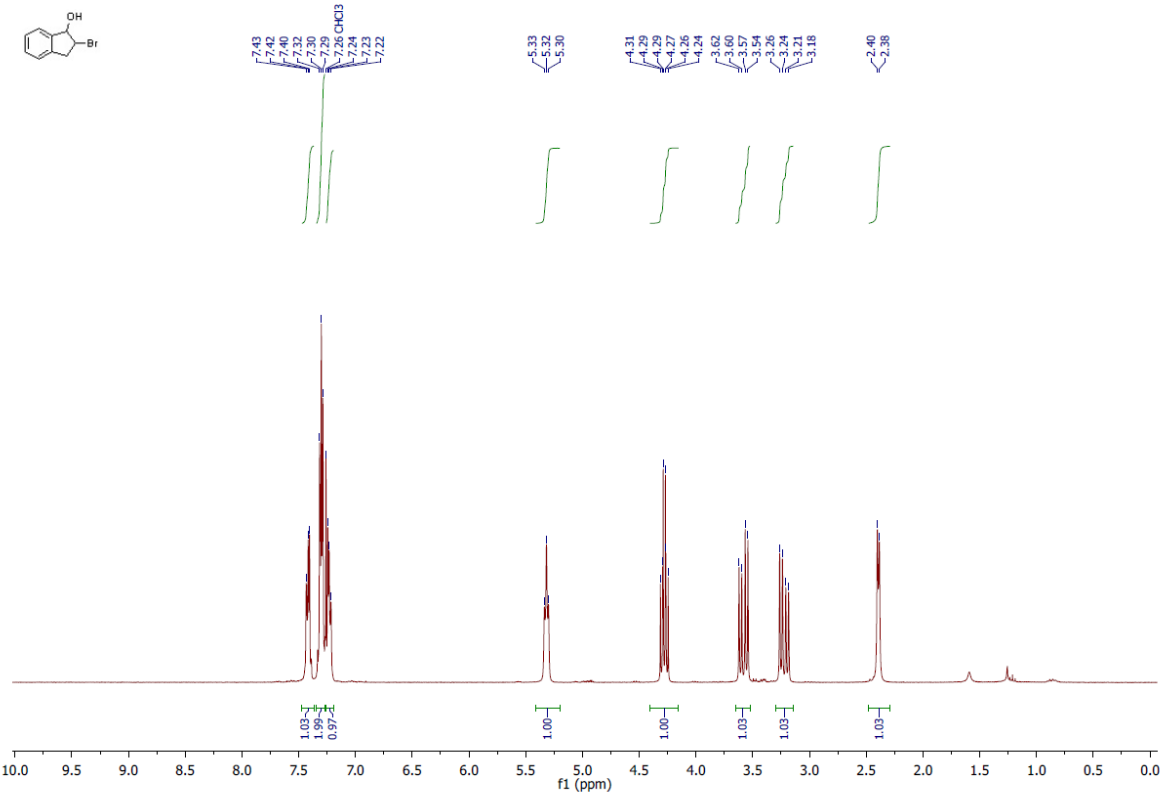
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-1-phenylpropan-1-ol (**3j**)



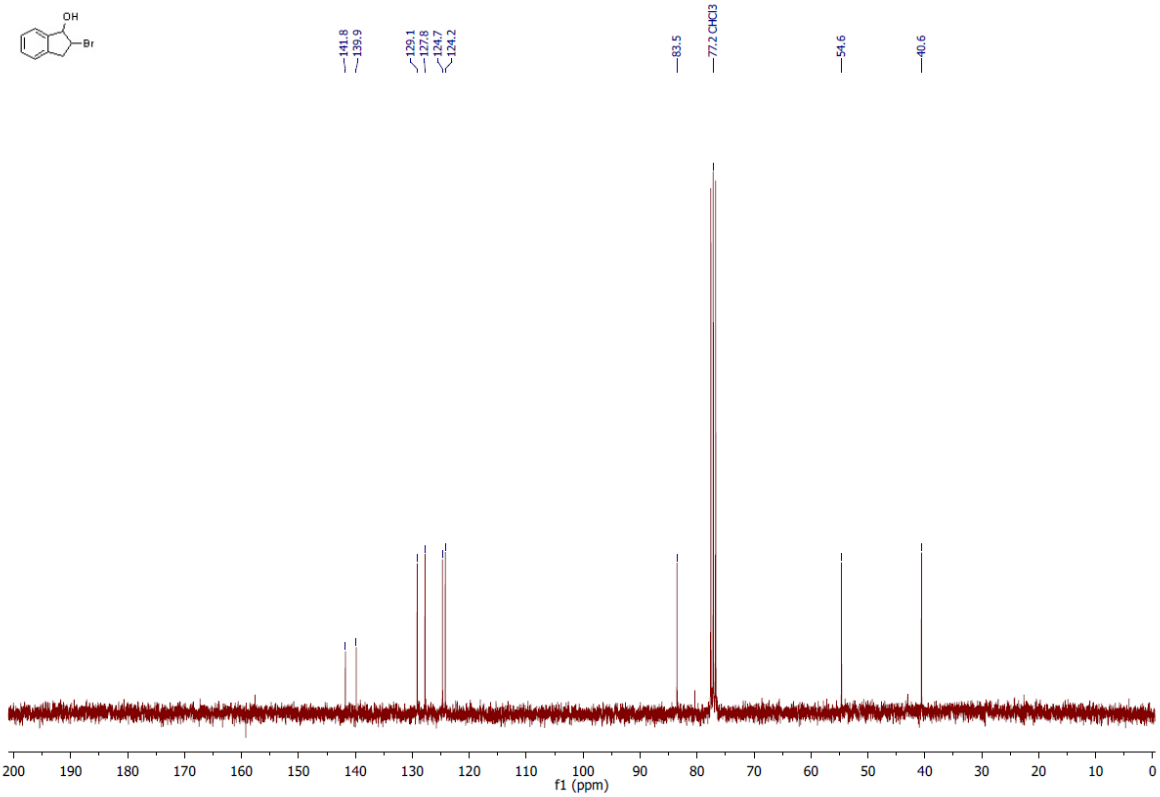
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-1-phenylpropan-1-ol (**3j**)



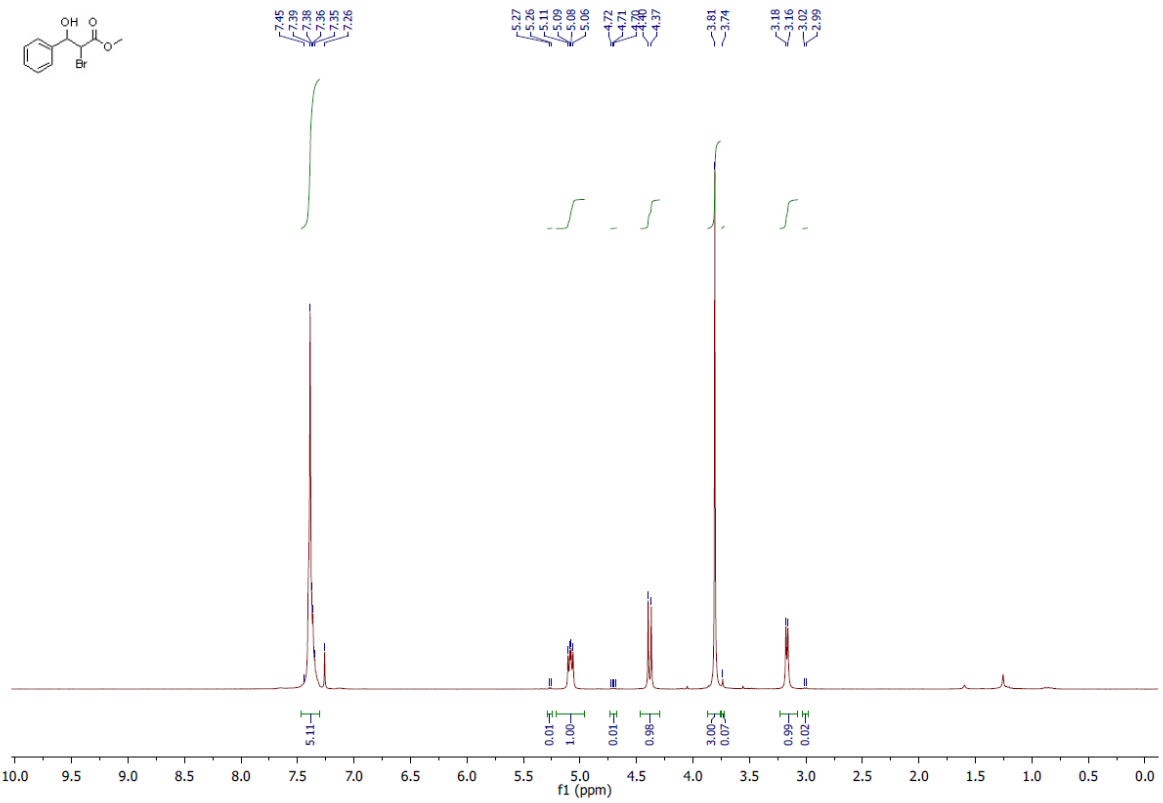
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-2,3-dihydro-1H-inden-1-ol (**3k**)



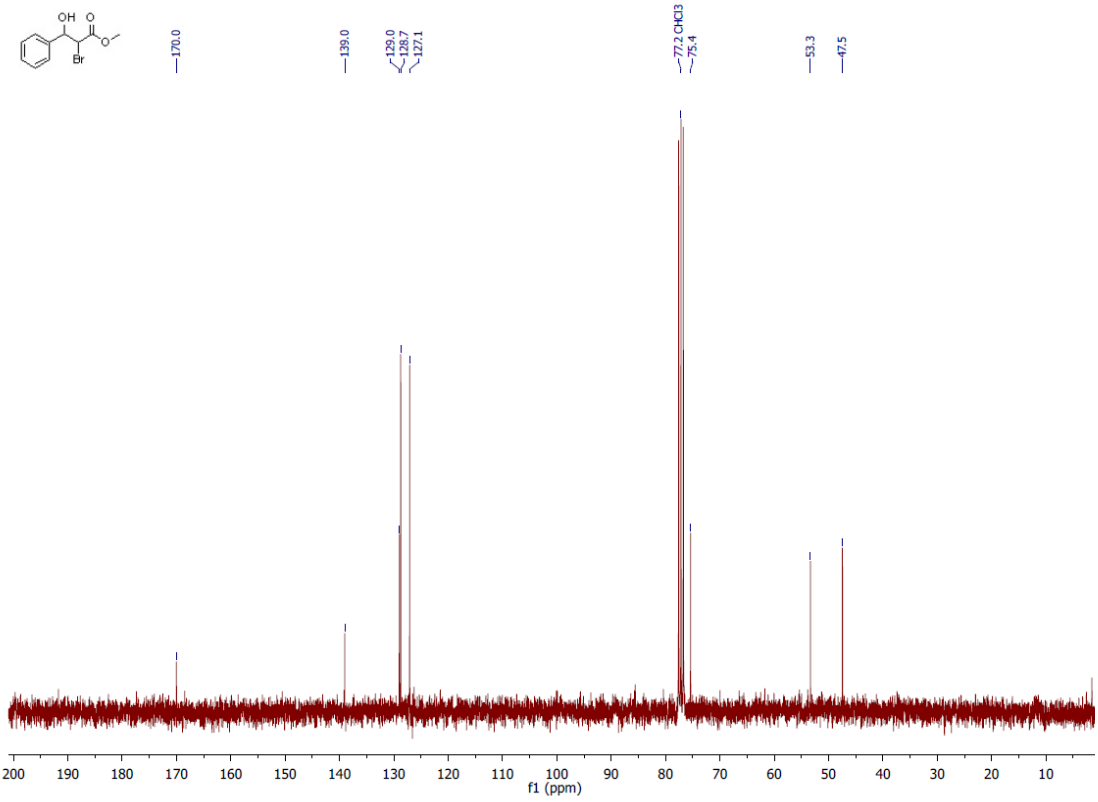
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-2,3-dihydro-1H-inden-1-ol (**3k**)



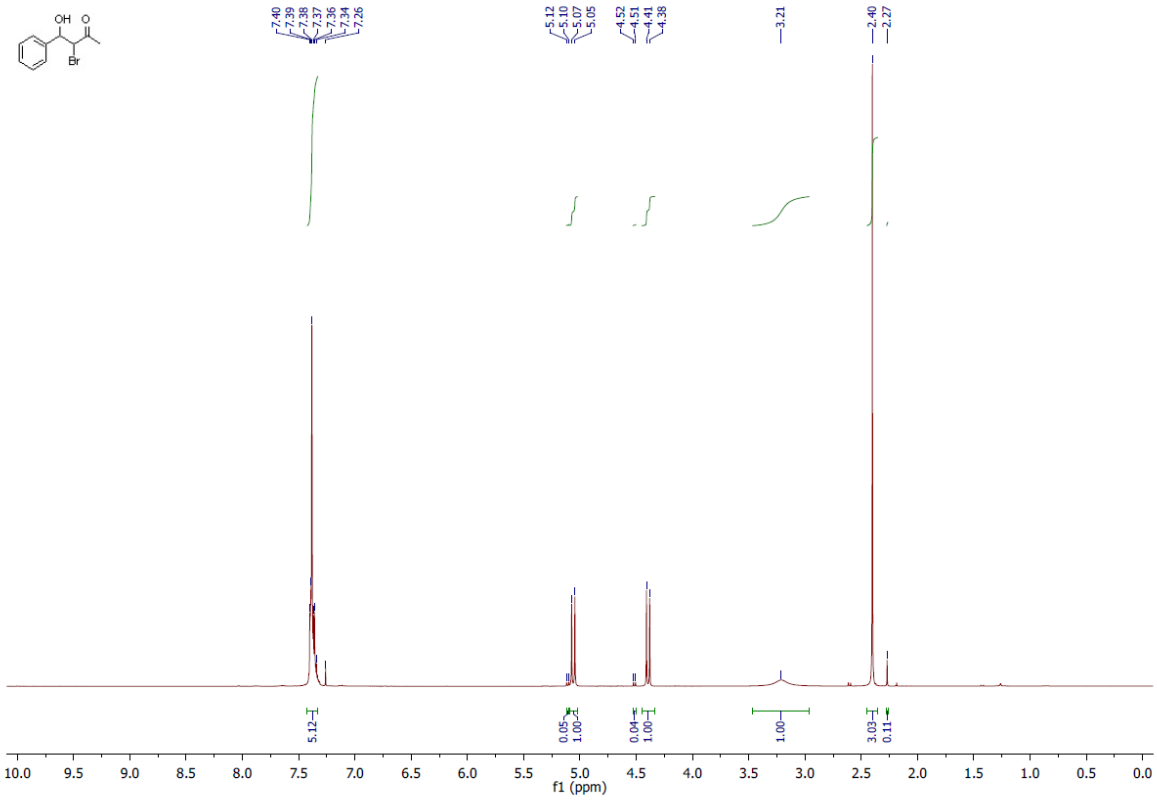
^{1}H NMR (300 MHz, $CDCl_3$) of methyl 2-bromo-3-hydroxy-3-phenylpropanoate (**3l**)



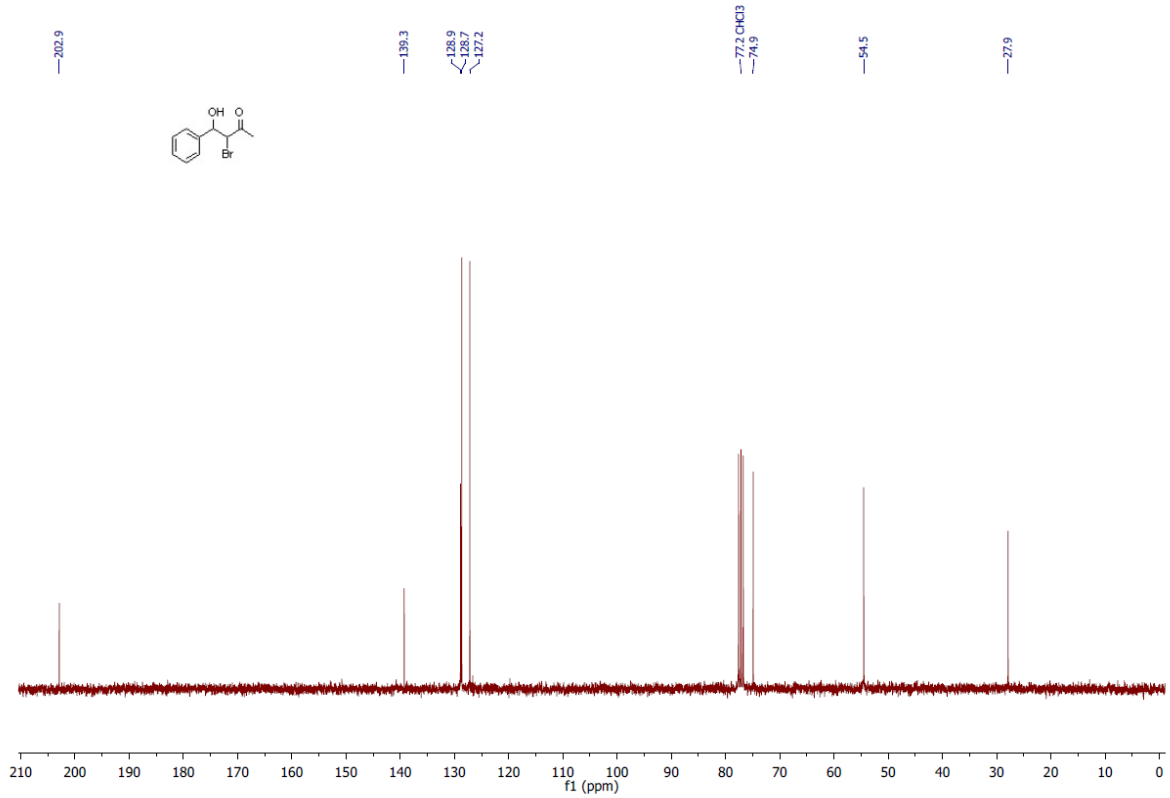
^{13}C NMR (75 MHz, $CDCl_3$) of methyl 2-bromo-3-hydroxy-3-phenylpropanoate (**3l**)



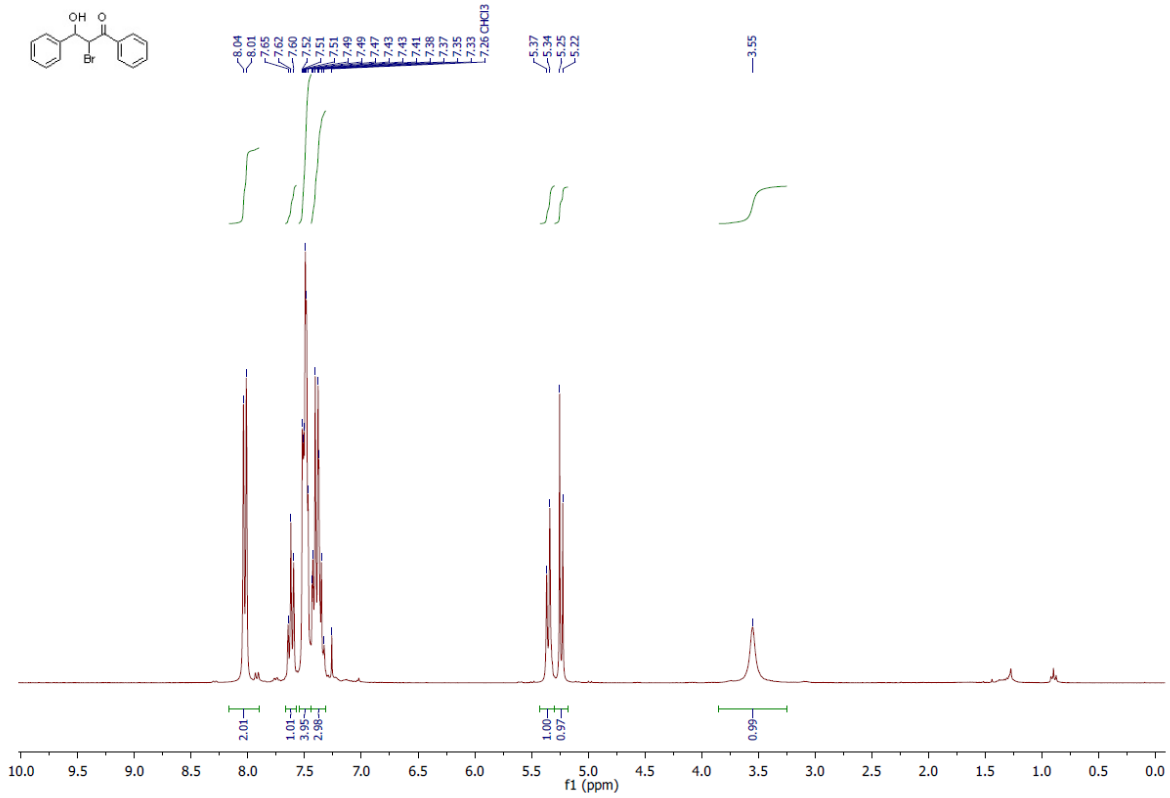
^{1}H NMR (300 MHz, $CDCl_3$) of 3-bromo-4-hydroxy-4-phenylbutan-2-one (**3m**)



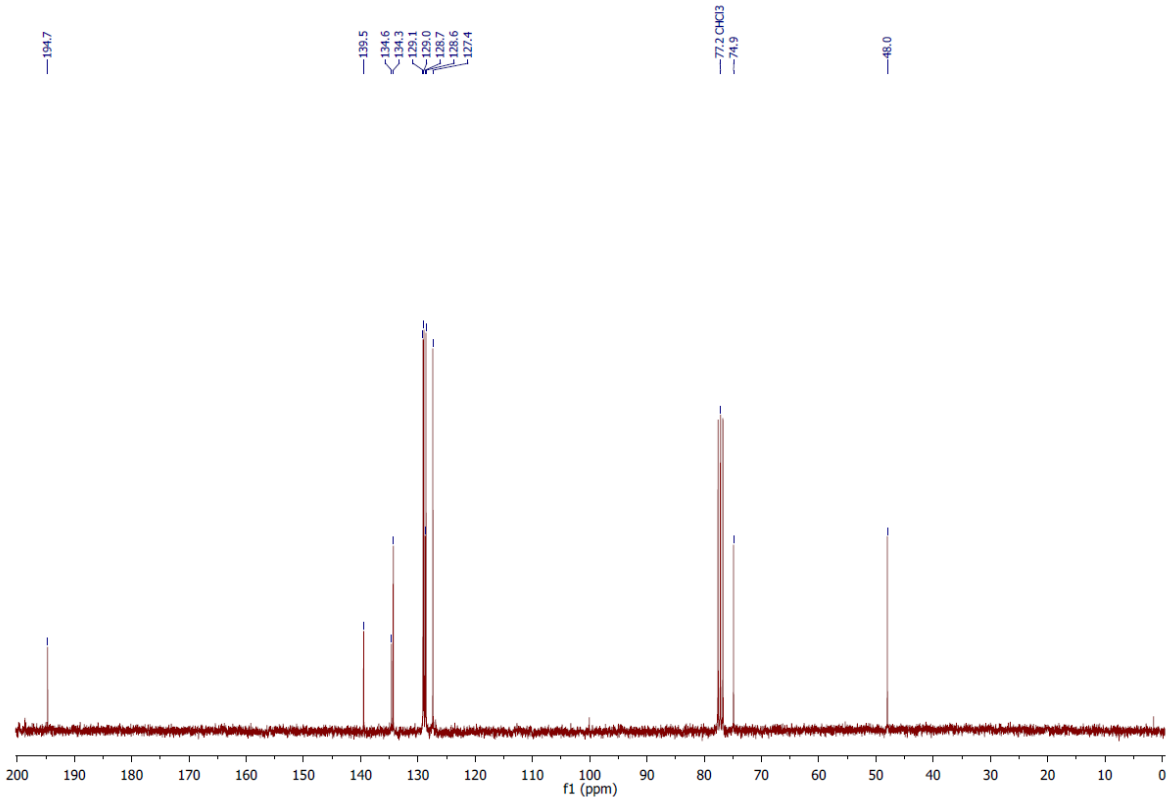
^{13}C NMR (75 MHz, $CDCl_3$) of 3-bromo-4-hydroxy-4-phenylbutan-2-one (**3m**)



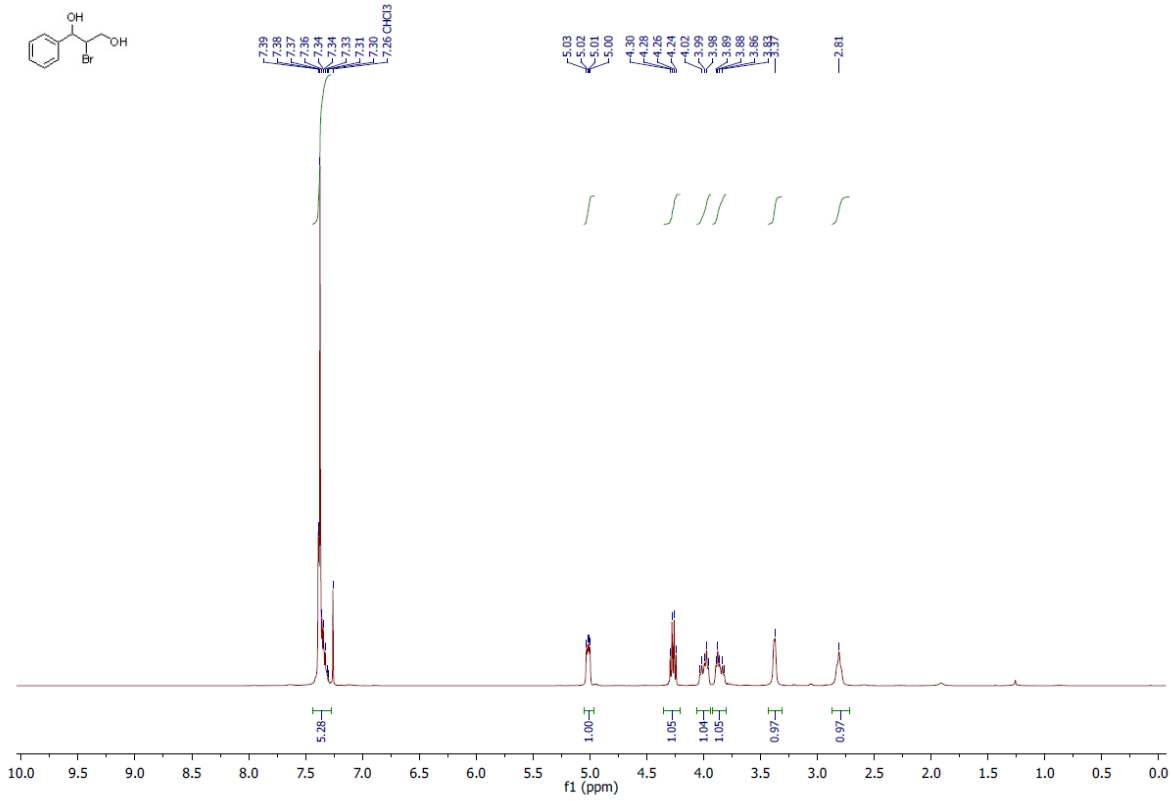
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-3-hydroxy-1,3-diphenylpropan-1-one (**3n**)



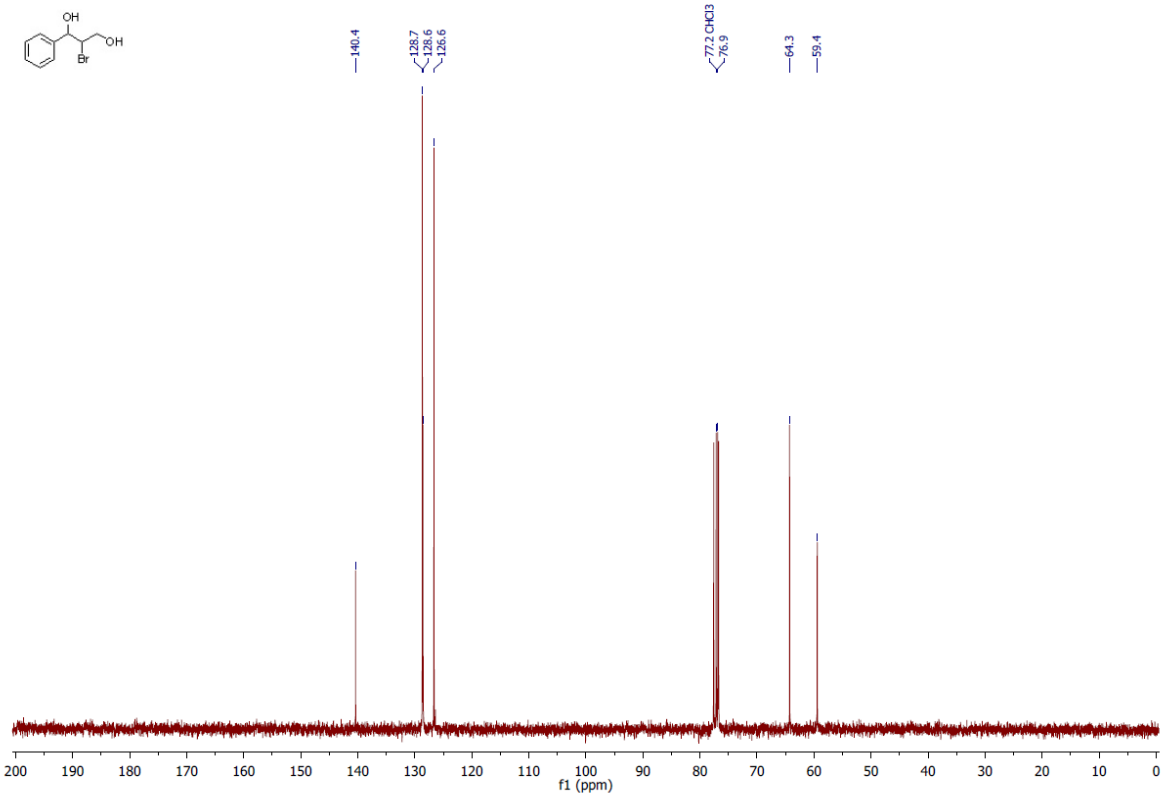
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-3-hydroxy-1,3-diphenylpropan-1-one (**3n**)



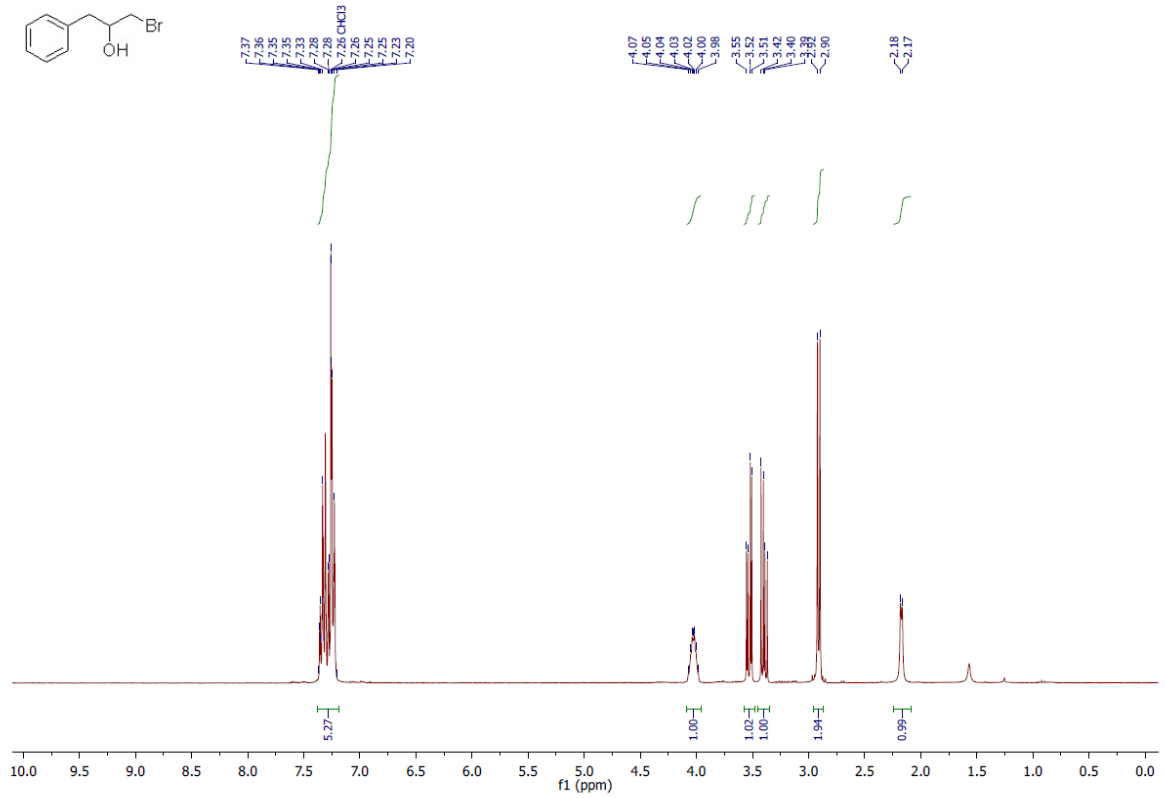
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-1-phenylpropane-1,3-diol (**3o**)



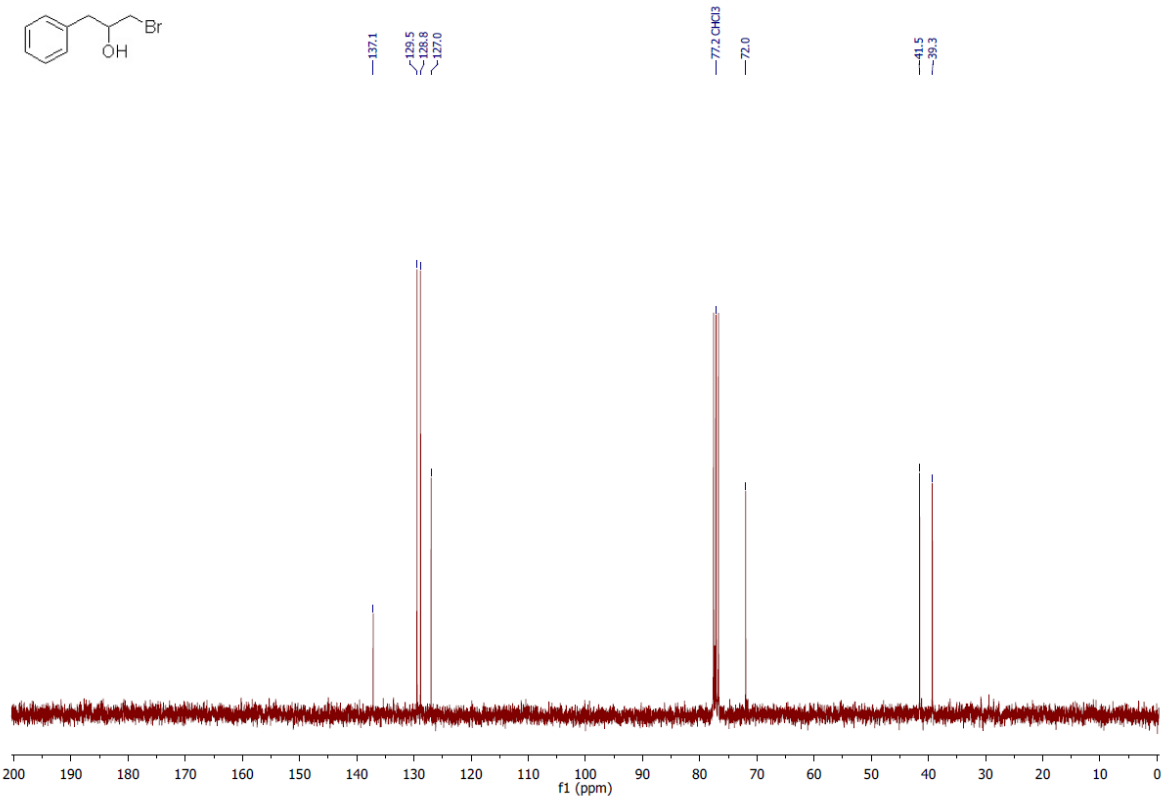
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromo-1-phenylpropane-1,3-diol (**3o**)



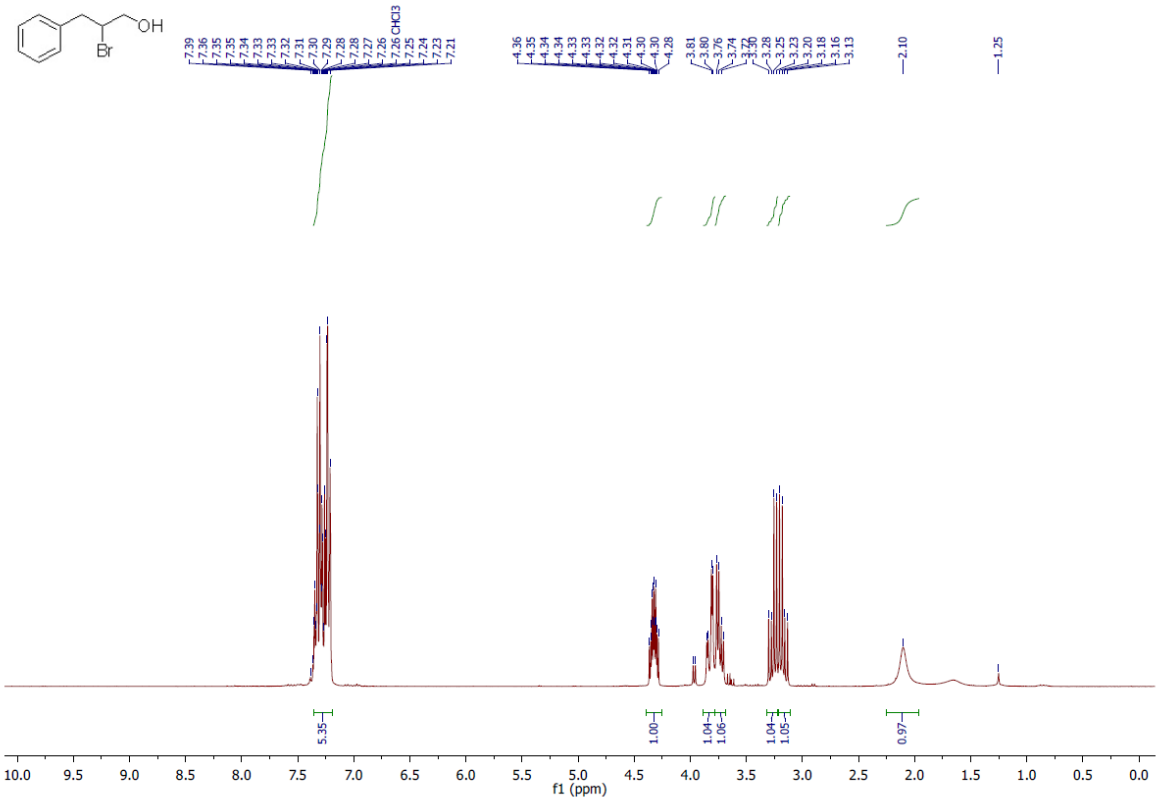
^{1}H NMR (300 MHz, $CDCl_3$) of 1-bromo-3-phenylpropan-2-ol (**3p**)



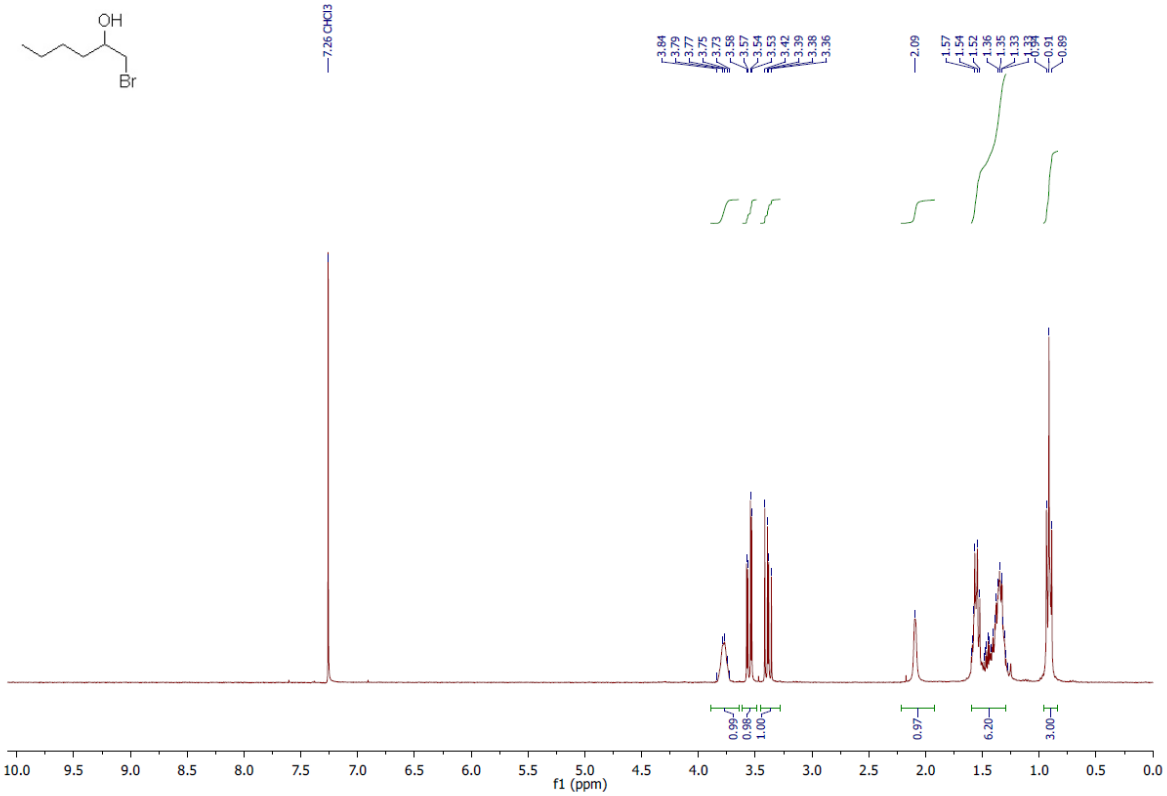
^{13}C NMR (75 MHz, $CDCl_3$) of 1-bromo-3-phenylpropan-2-ol (**3p**)



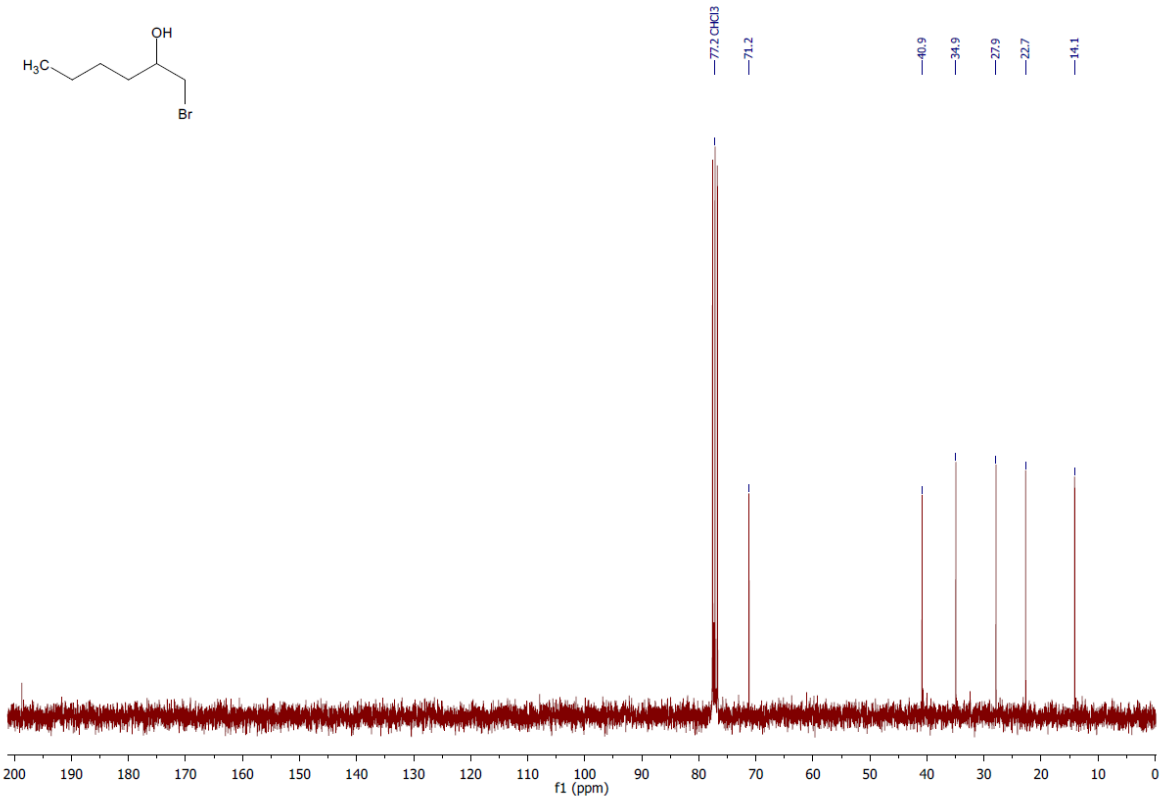
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromo-3-phenylpropan-1-ol (**3p'**)



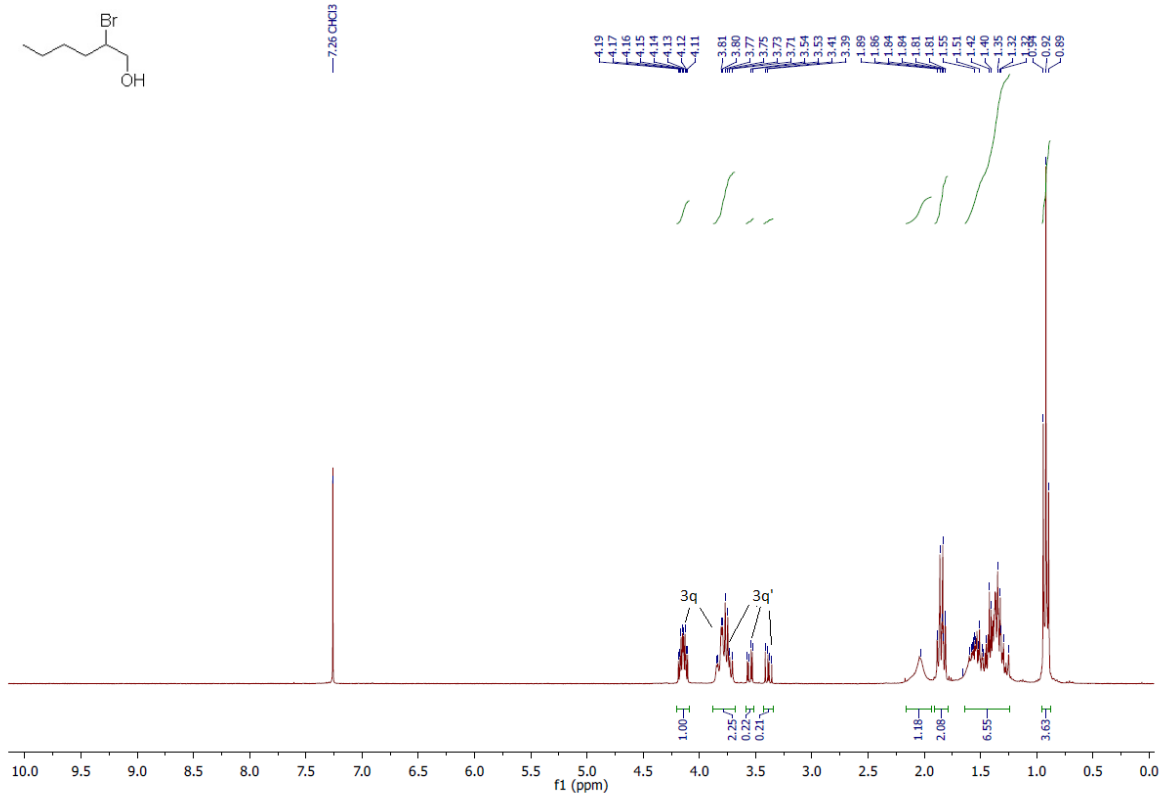
^{1}H NMR (300 MHz, $CDCl_3$) of 1-bromohexan-2-ol (**3q**)



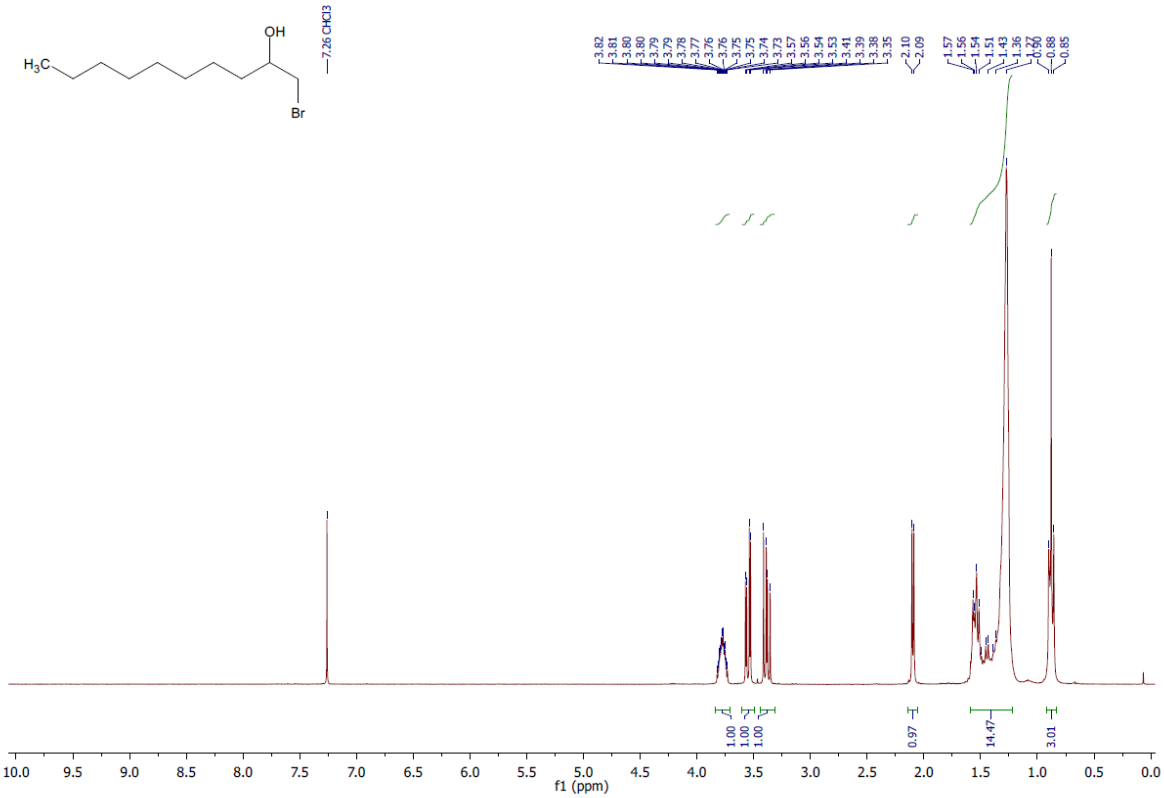
^{13}C NMR (75 MHz, $CDCl_3$) of 1-bromohexan-2-ol (**3q**)



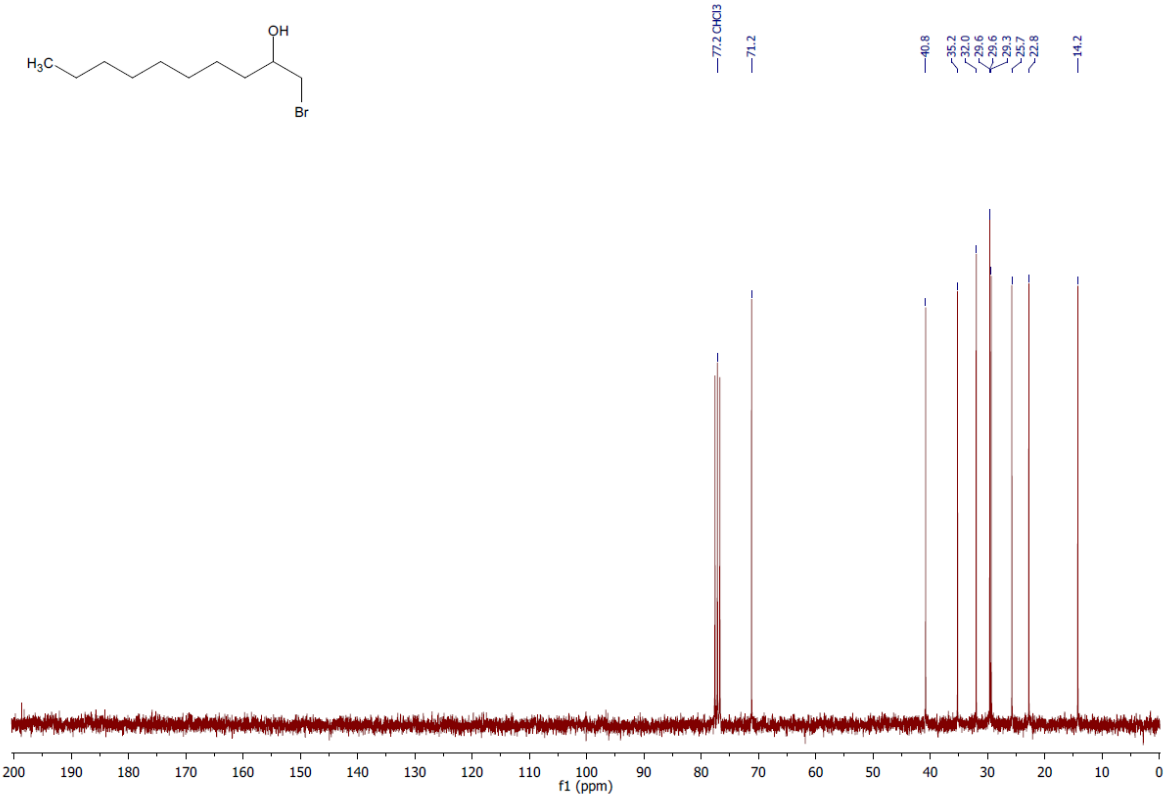
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromohexan-1-ol (**3q'**)



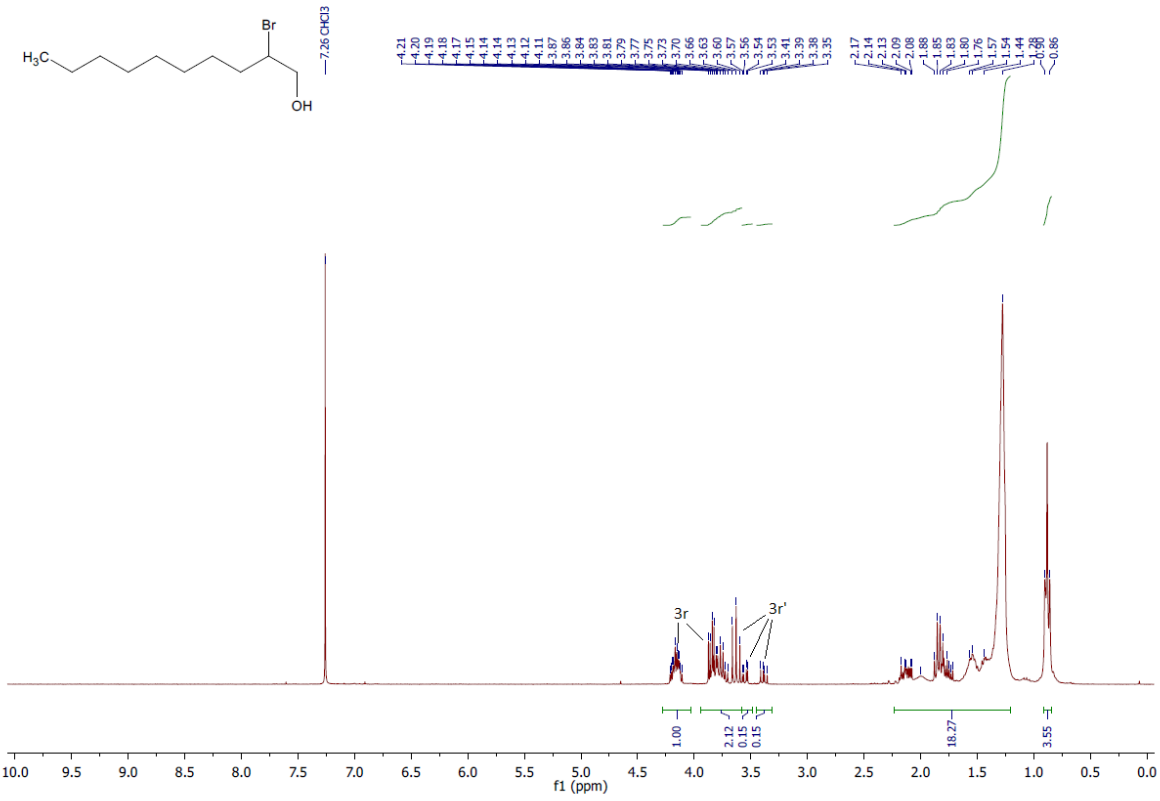
^{1}H NMR (300 MHz, $CDCl_3$) of 1-bromodecan-2-ol (**3r**)



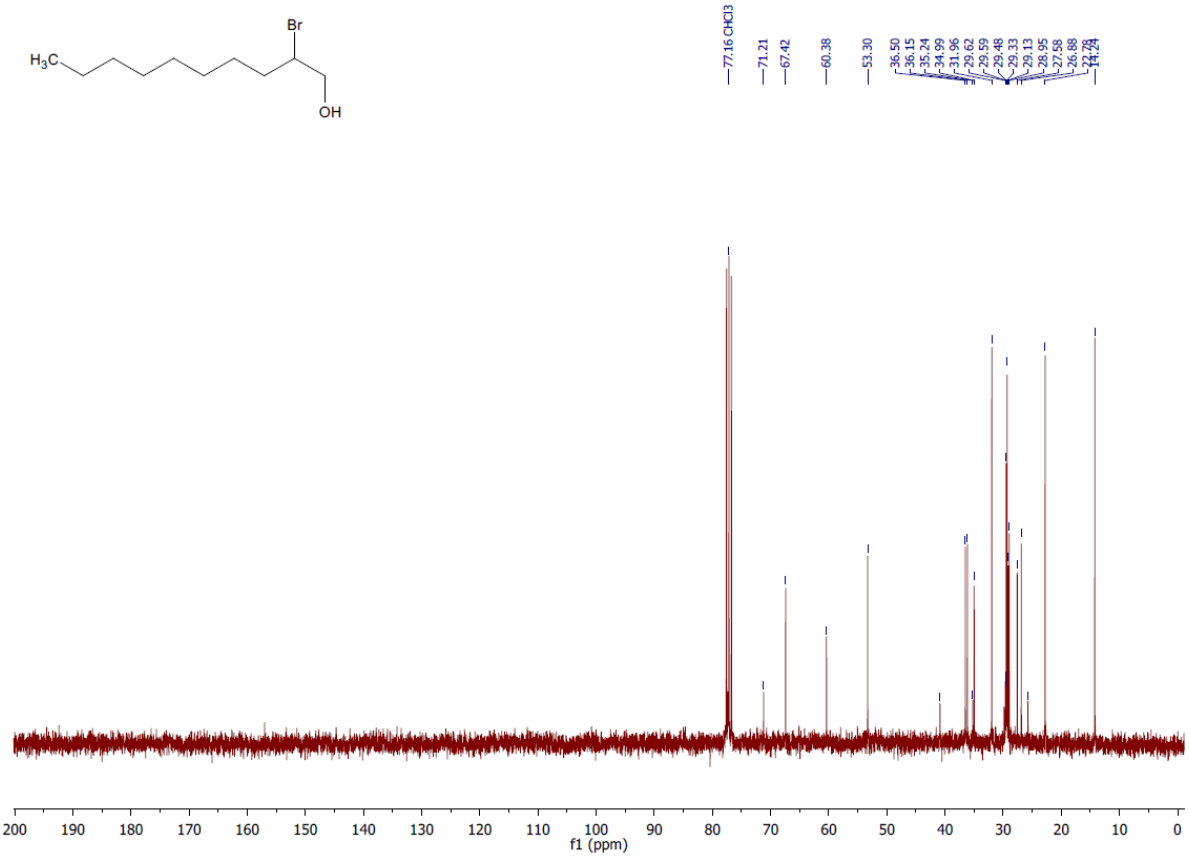
^{13}C NMR (75 MHz, $CDCl_3$) of 1-bromodecan-2-ol (**3r**)



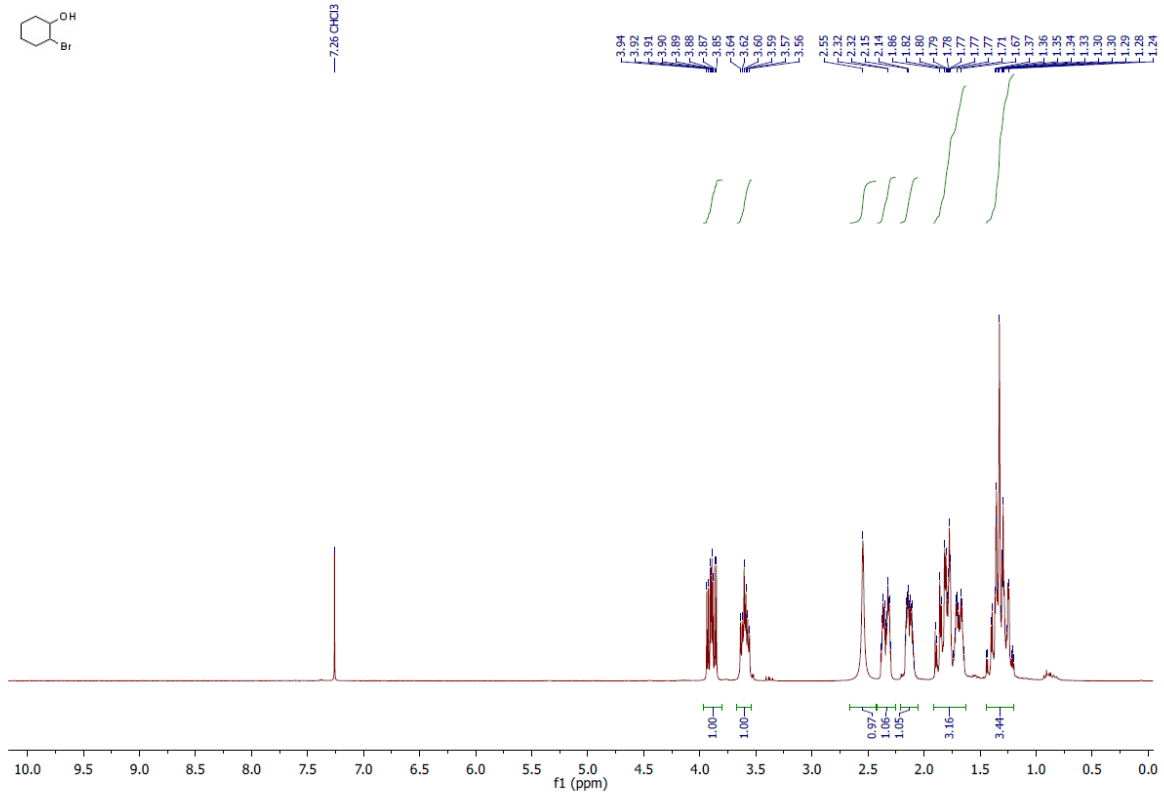
^{1}H NMR (300 MHz, $CDCl_3$) of 2-bromodecan-1-ol (**3r'**)



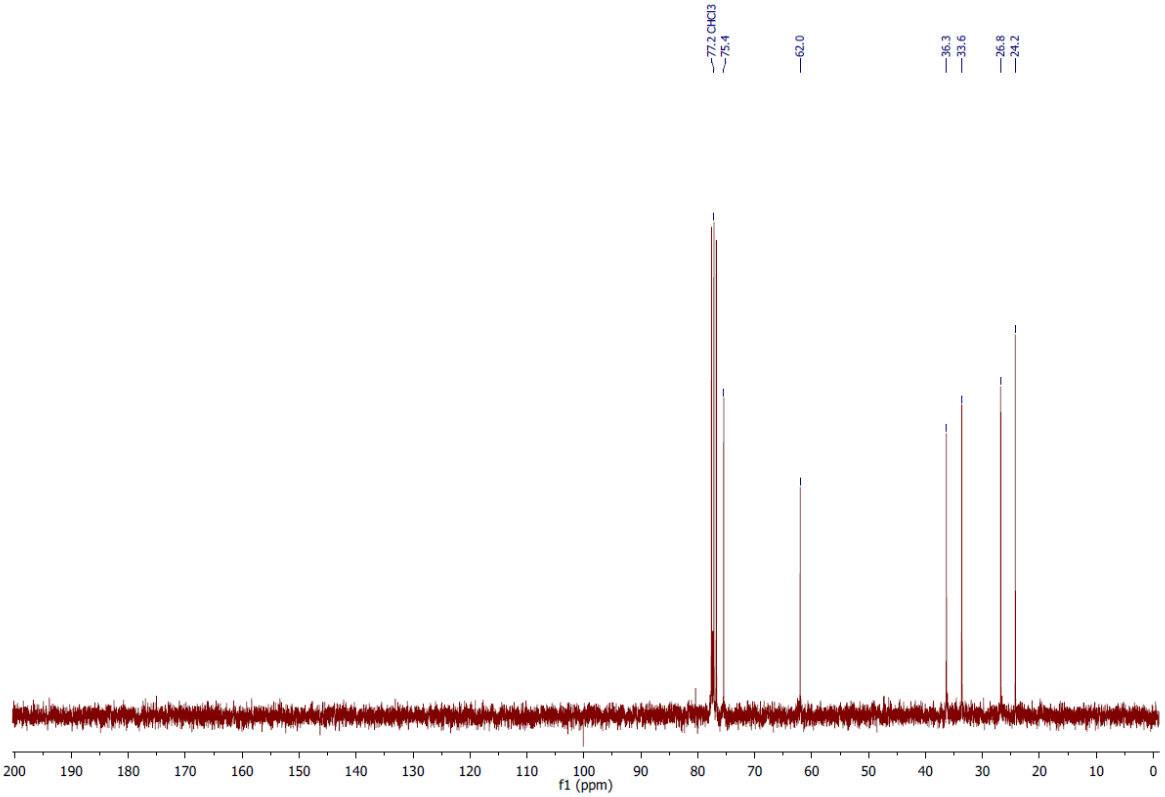
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromodecan-1-ol (**3r'**)



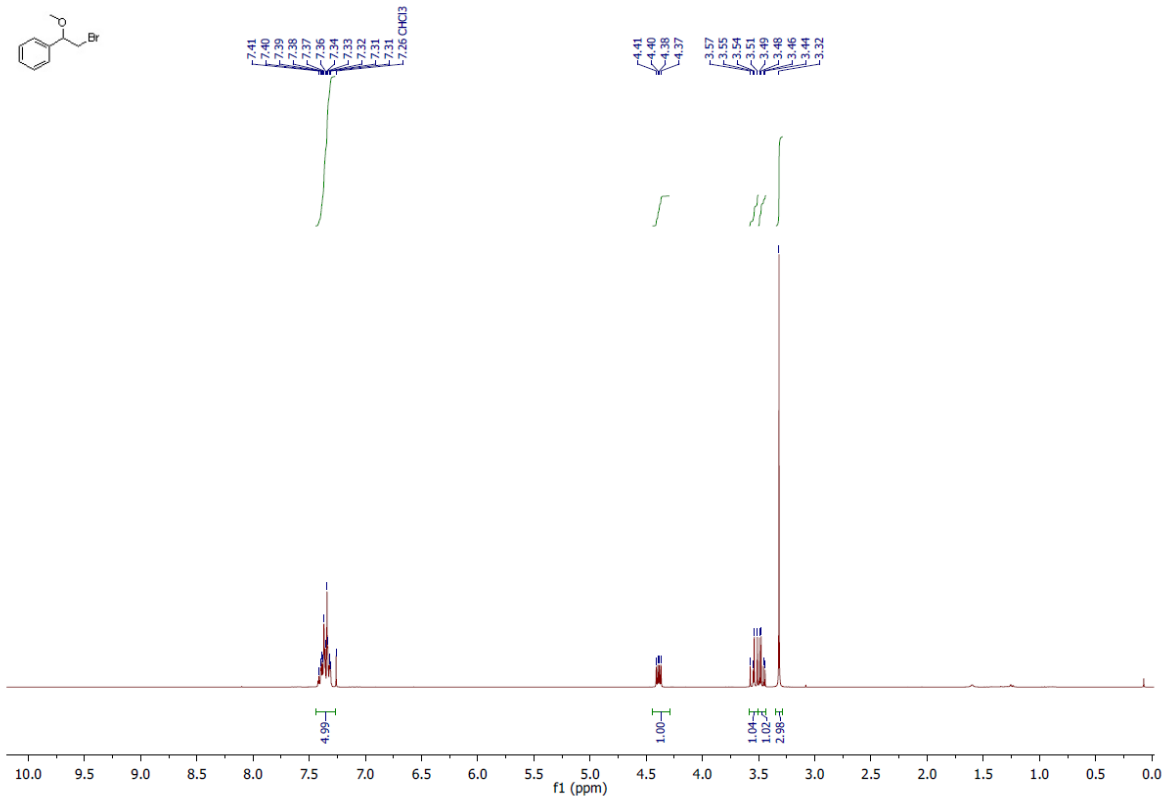
^{1}H NMR (300 MHz, $CDCl_3$) 2-bromocyclohexan-1-ol (**3s**)



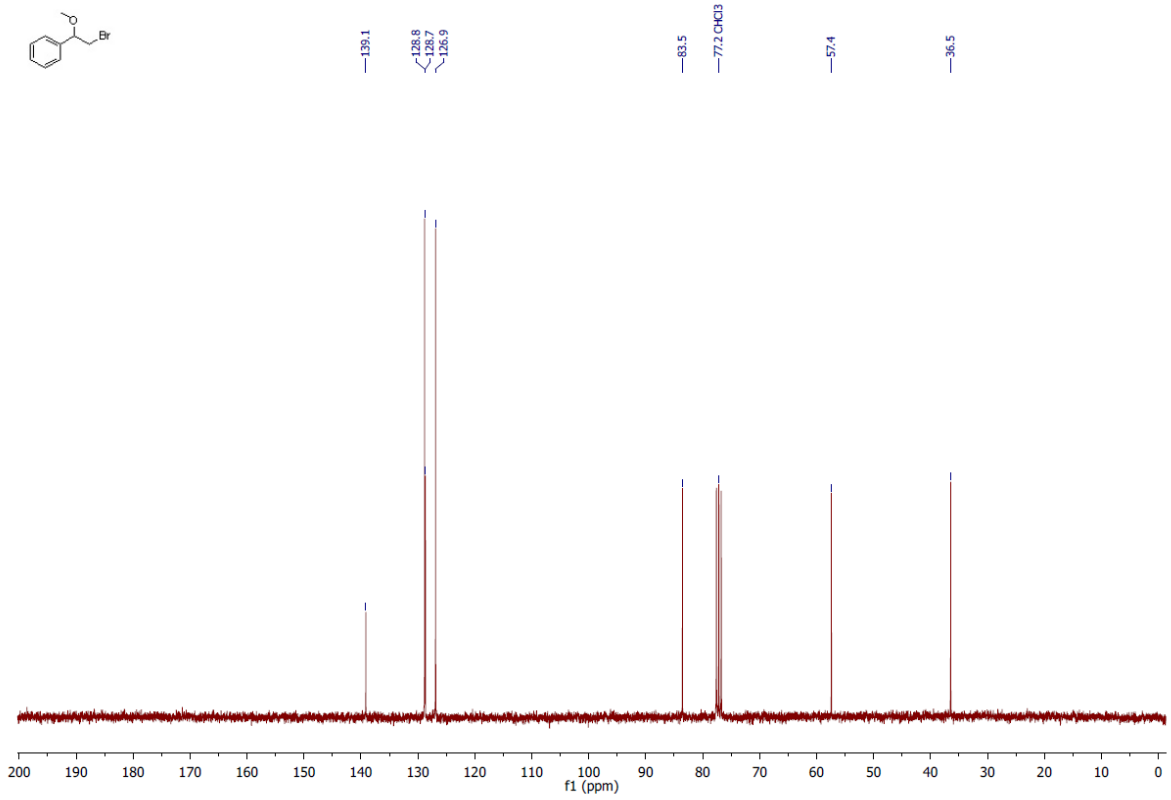
^{13}C NMR (75 MHz, $CDCl_3$) of 2-bromocyclohexan-1-ol (**3s**)



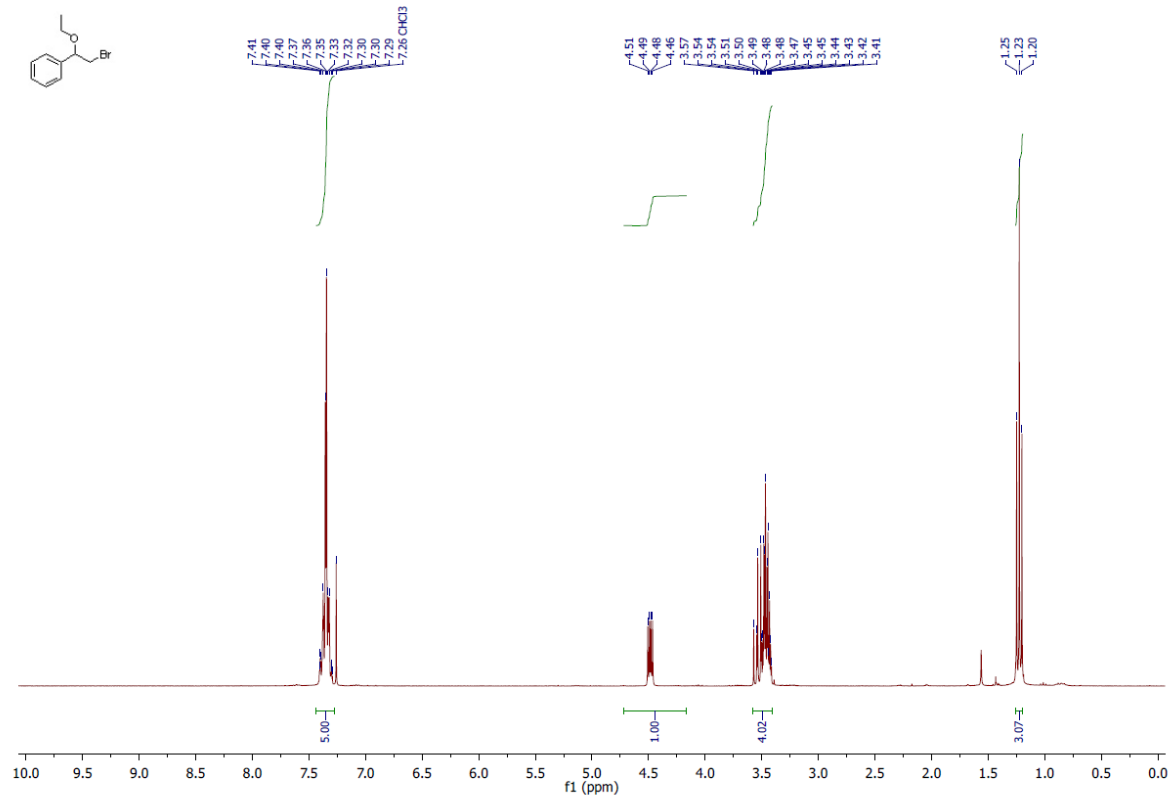
^{1}H NMR (300 MHz, $CDCl_3$) of (2-bromo-1-methoxyethyl)benzene (**4a**)



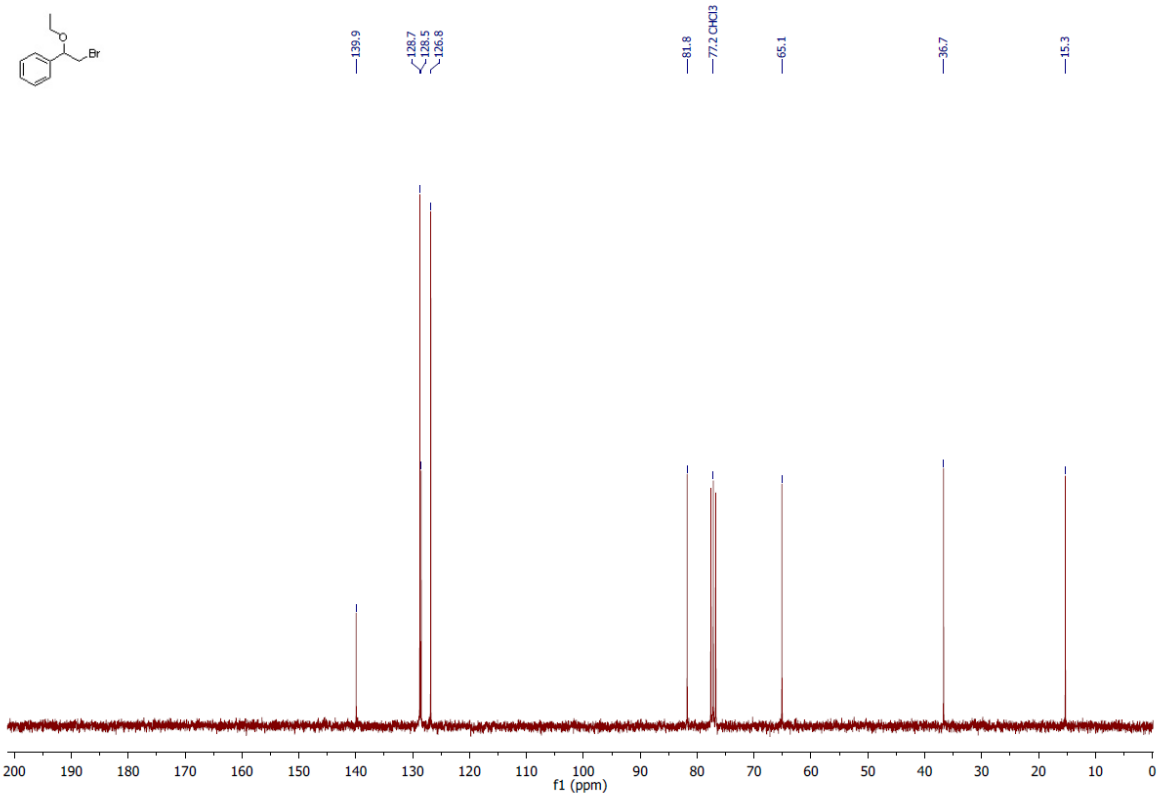
^{13}C NMR (75 MHz, $CDCl_3$) of (2-bromo-1-methoxyethyl)benzene (**4a**)



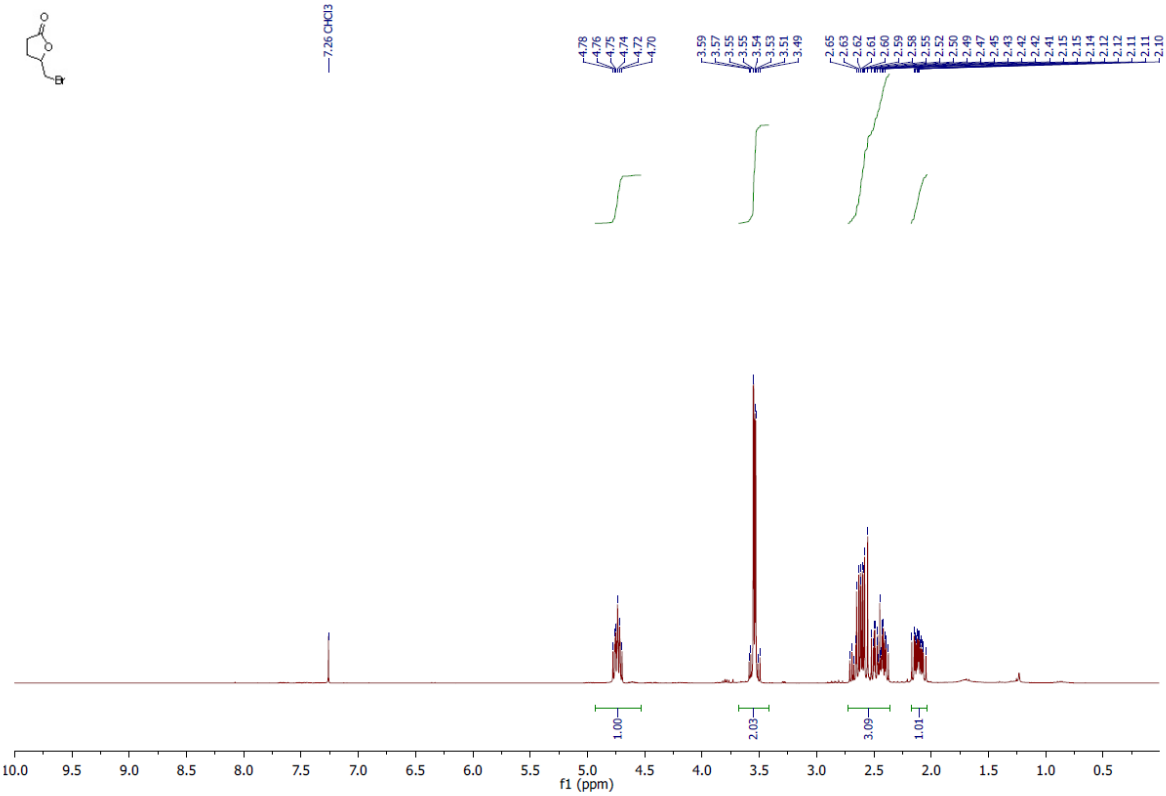
^{1}H NMR (300 MHz, $CDCl_3$) of (2-bromo-1-ethoxyethyl)benzene (**4b**)



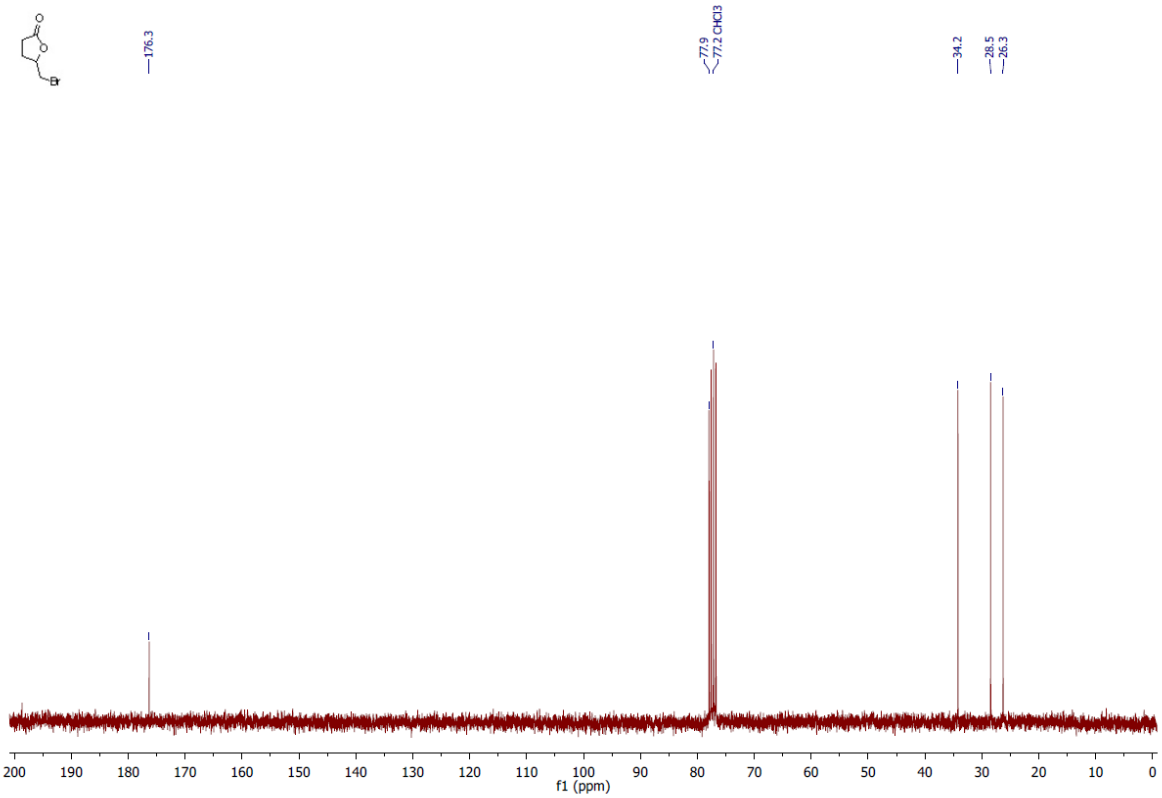
^{13}C NMR (75 MHz, $CDCl_3$) of (2-bromo-1-ethoxyethyl)benzene (**4b**)



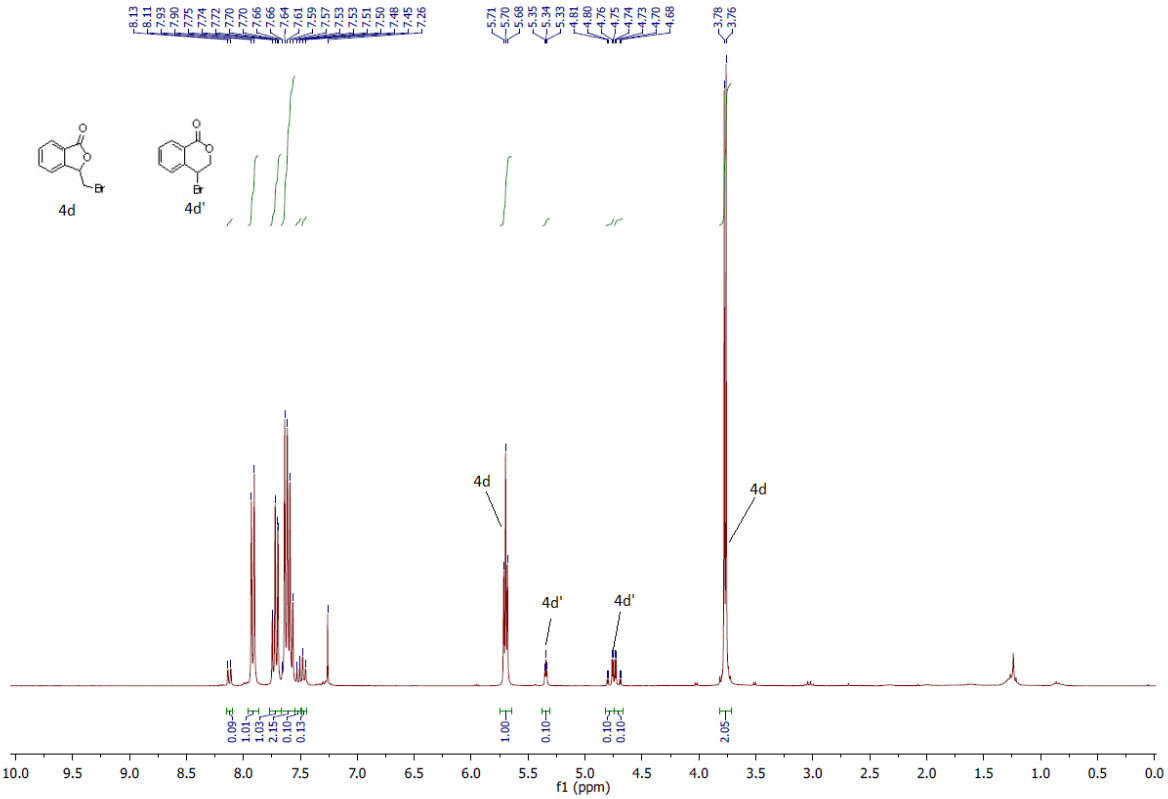
^{1}H NMR (300 MHz, $CDCl_3$) of 5-(bromomethyl)dihydrofuran-2(3H)-one (**4c**)



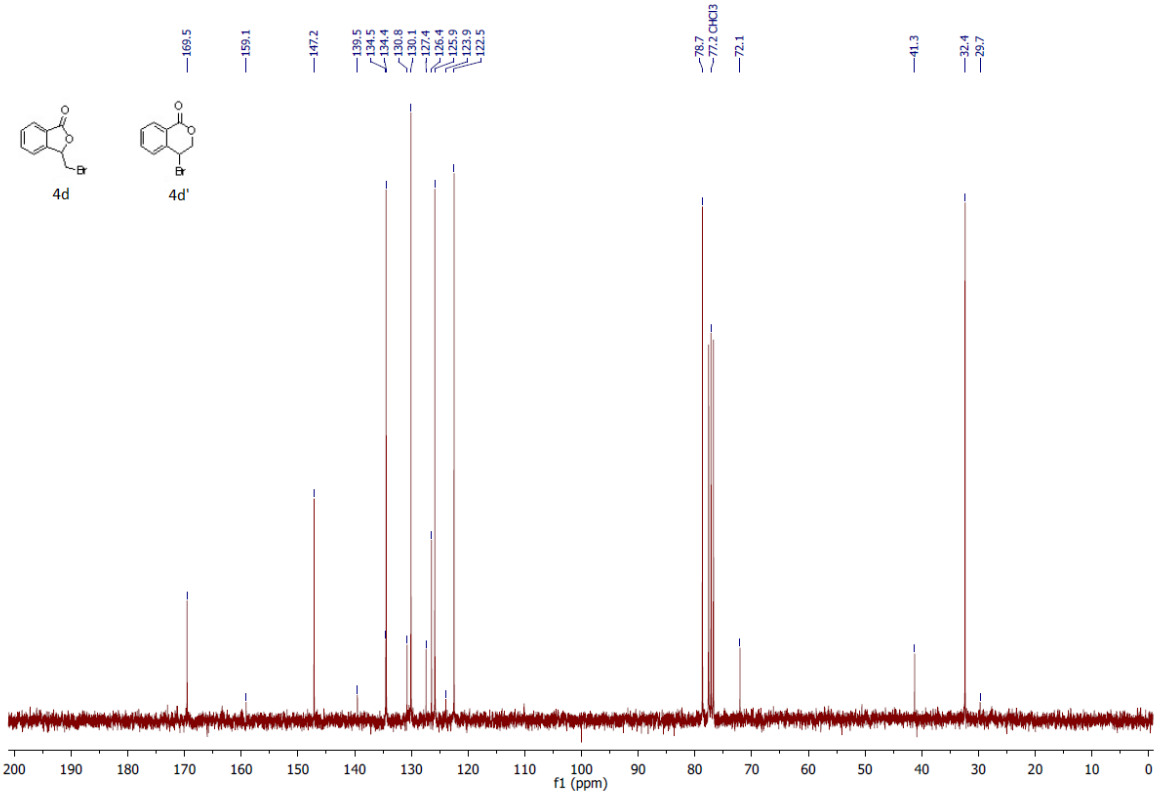
^{13}C NMR (75 MHz, $CDCl_3$) of 5-(bromomethyl)dihydrofuran-2(3H)-one (**4c**)



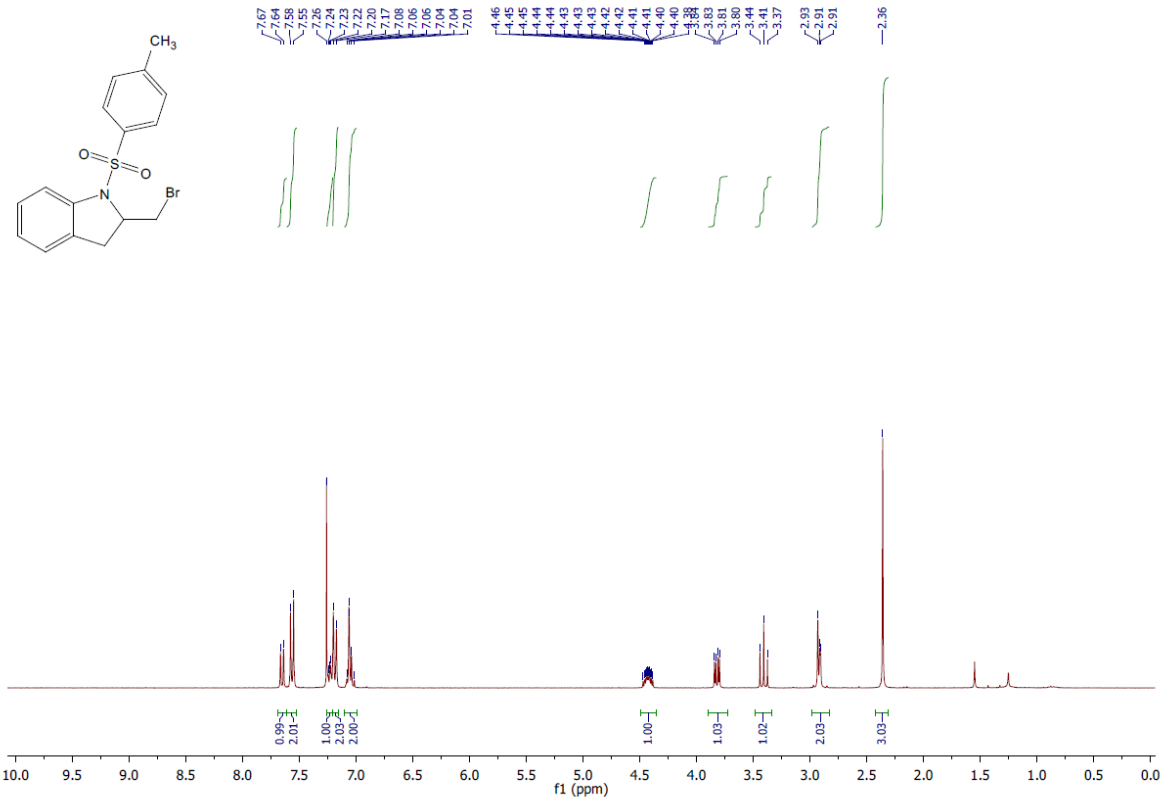
^{1}H NMR (300 MHz, $CDCl_3$) of 3-(bromomethyl)isobenzofuran-1(3H)-one (**4d**) & 4-bromoisochroman-1-one (**4d'**)



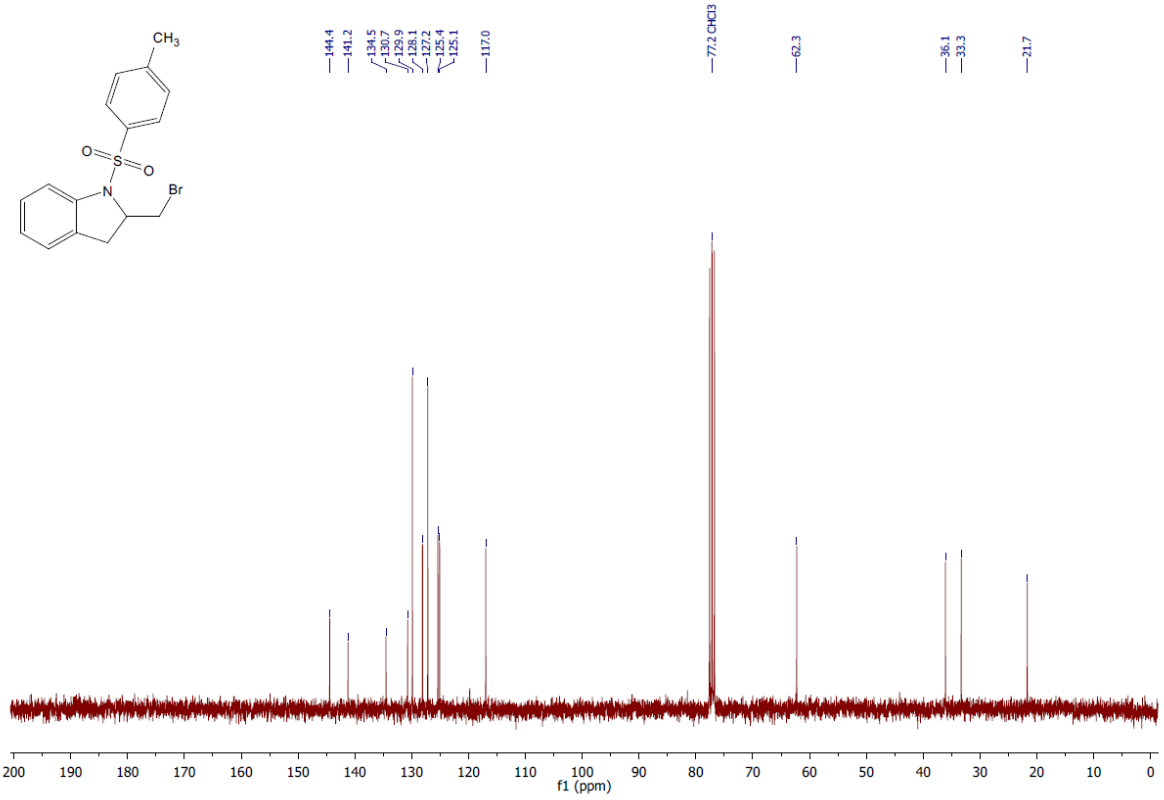
^{13}C NMR (75 MHz, $CDCl_3$) of 3-(bromomethyl)isobenzofuran-1(3H)-one (**4d**) & 4-bromoisochroman-1-one (**4d'**)



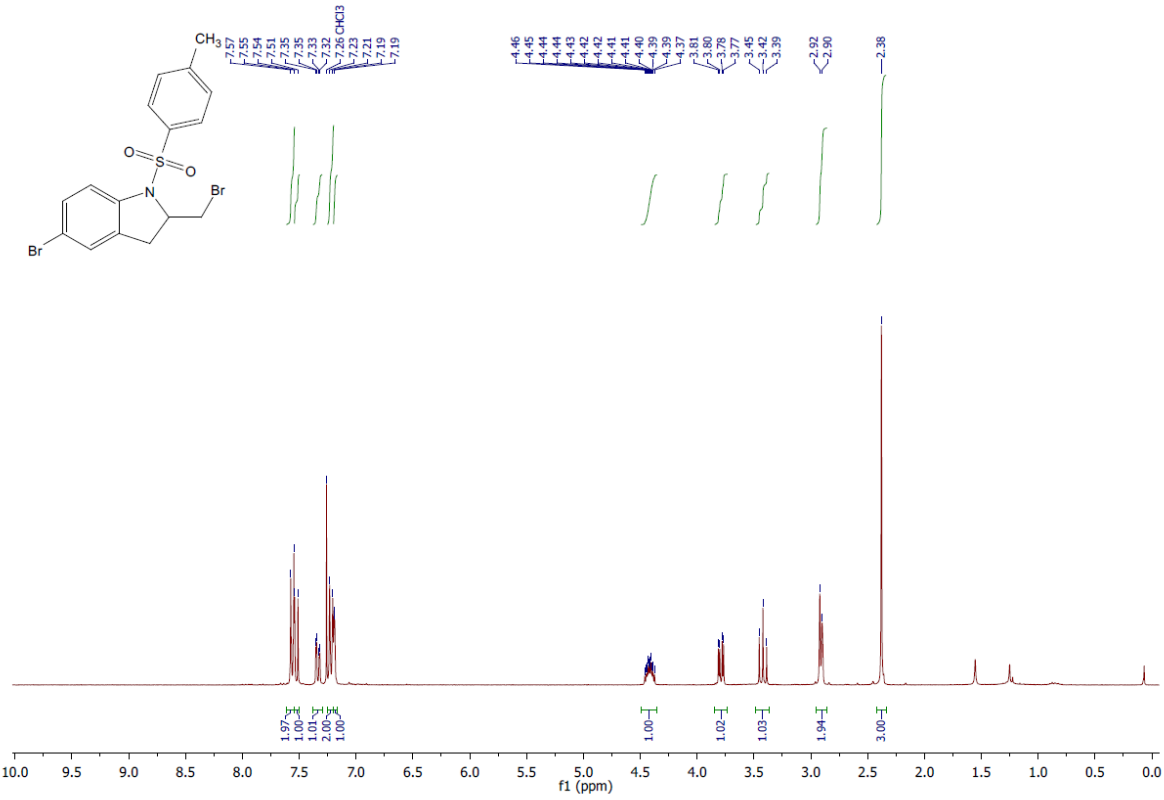
^{1}H NMR (300 MHz, $CDCl_3$) of 2-(bromomethyl)-1-tosylindoline (**4e**)



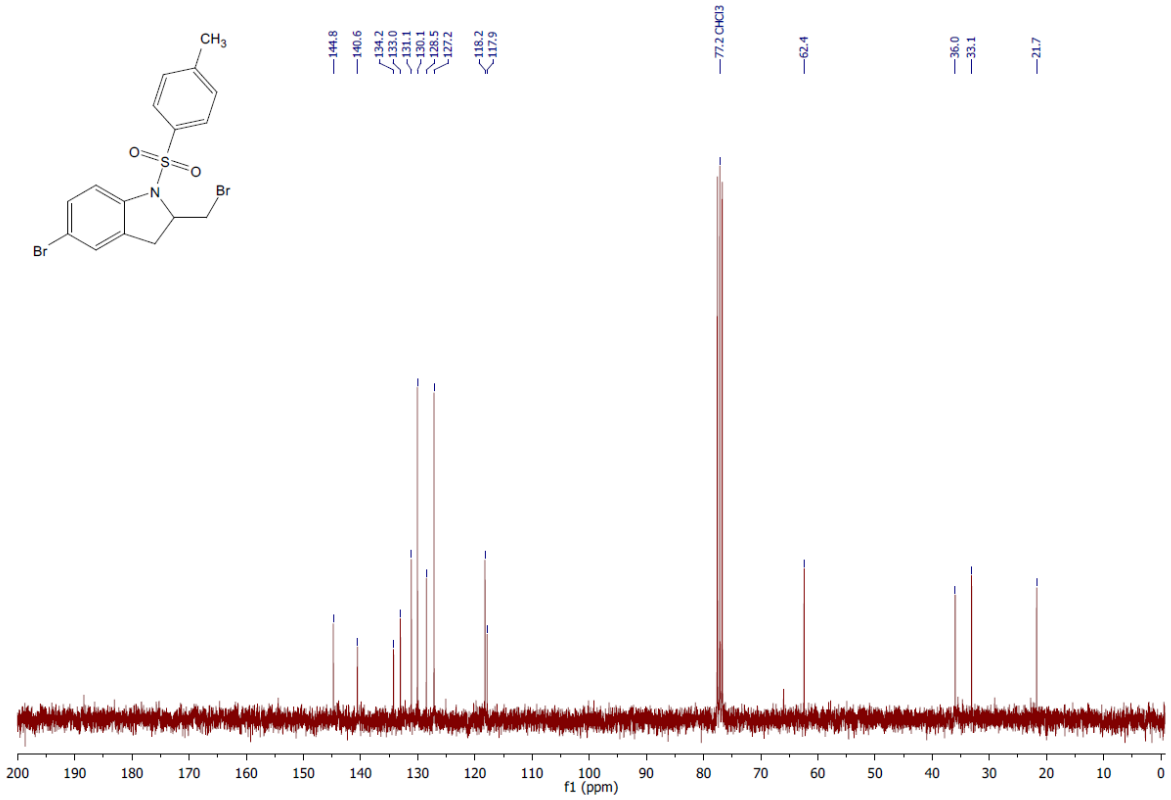
^{13}C NMR (75 MHz, $CDCl_3$) of 2-(bromomethyl)-1-tosylindoline (**4e**)



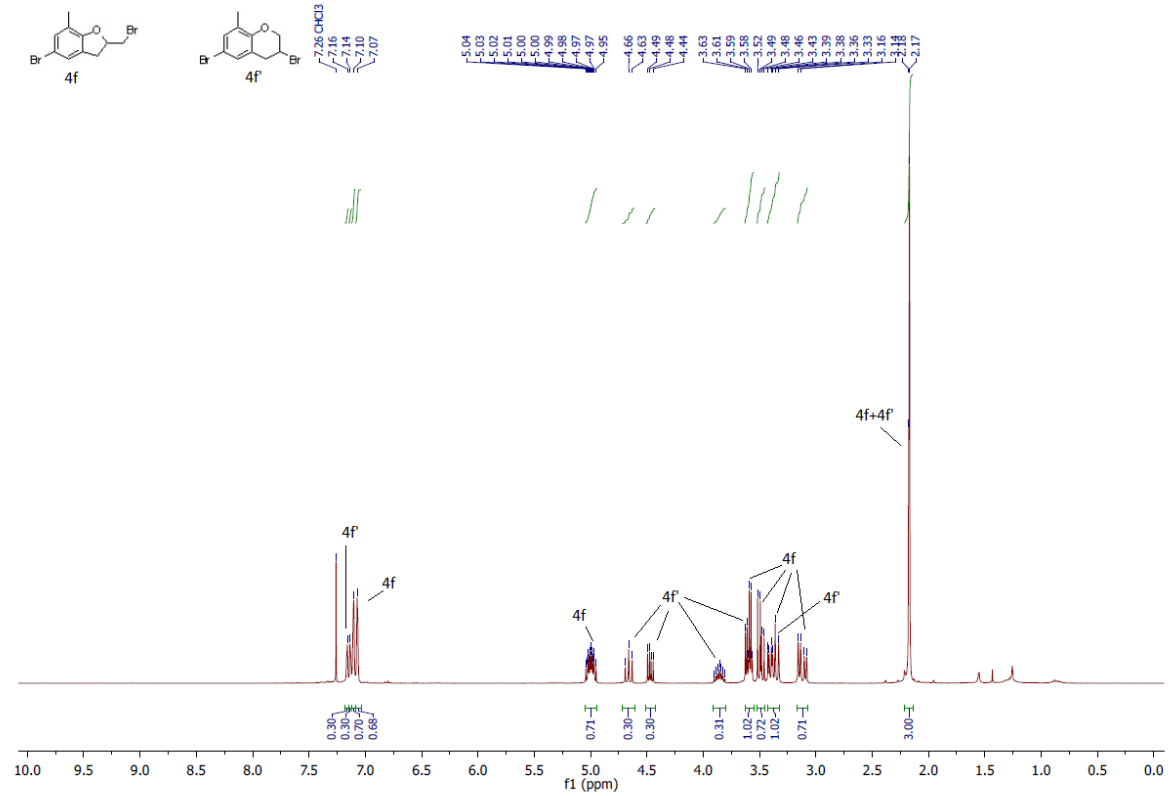
^{1}H NMR (300 MHz, $CDCl_3$) of 5-bromo-2-(bromomethyl)-1-tosylindoline (**4e'**)



^{13}C NMR (75 MHz, $CDCl_3$) of 5-bromo-2-(bromomethyl)-1-tosylindoline (**4e'**)



^{1}H NMR (300 MHz, $CDCl_3$) of 5-bromo-2-(bromomethyl)-7-methyl-2,3-dihydrobenzofuran (**4f**) & 3,6-dibromo-8-methylchromane (**4f'**)



^{13}C NMR (75 MHz, $CDCl_3$) of 5-bromo-2-(bromomethyl)-7-methyl-2,3-dihydrobenzofuran (**4f**) & 3,6-dibromo-8-methylchromane (**4f'**)