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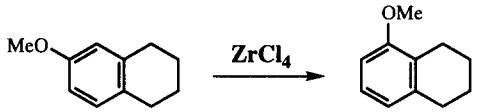
The Sliding Cyclohexane Rearrangement

David C. Harrowven* and Richard F. Dainty

Department of Chemistry, The University, Southampton, S017 1BJ.

Abstract: 6-methoxytetralins may be transformed into 8-methoxytetralins through the action of zirconium tetrachloride. Yields are generally good though turnover is slow. Ultrasonic irradiation, phase transfer catalysts, crown ethers and lithium chloride all accelerate the reaction which proceeds *via* scission of the C-1 to C-8a bond and cyclisation by intramolecular Friedel-Crafts alkylation.

We recently reported a new rearrangement mediated by zirconium(IV) chloride.[1] In essence, simply stirring a chloroform solution of 6-methoxytetralin **1** with $ZrCl_4$ at ambient temperature effected isomerisation to 8-methoxytetralin **2**.[2] One disappointing feature was the slow reaction rate; 18 hours being required to achieve a 50% conversion for the transformation of **1** to **2**. In this paper we describe full details of the rearrangement and highlight two developments that have greatly improved its efficiency.



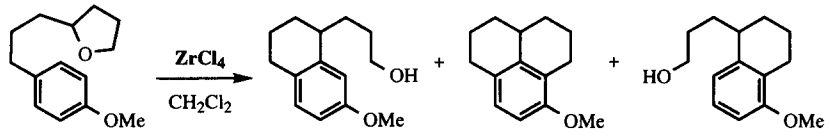
1 **2**

Scheme 1

The rearrangement was discovered during an investigation into the intramolecular alkylation of arenes by higher cyclic ethers. Our goal was to establish conditions for the direct conversion of tetrahydrofurans such as **3** to tetralins and hexahydrophenalenes. The first objective, **3** → **4**, was realised in 71% yield through the action of titanium(IV) chloride,[3] however, extension of the method to the sequential cyclisation **3** → **5** proved intractable.[4] Exposure of **3** to hard Lewis acids generally led to extensive decomposition while treatment with soft Lewis acids returned the starting material on work up.

Preliminary studies using zirconium(IV) chloride gave some encouragement. Modest yields of tetralin **4** (~50%) could be realised when chloroform solutions of **3** were exposed to a five fold excess of $ZrCl_4$ for short periods (2 h). After 24 hours, traces of the desired hexahydrophenalene **5** were also observed (10 %), though most of the remaining mass balance was accounted for by two isomeric tetralins, the anticipated intermediate **4** (43%) and a skeletally rearranged product **6** (34%). Conducting the experiment over 2 days had little effect on the yield of **5** (12%); however, a change in the ratio of tetralin **4** (14%) to tetralin **6** (59%) led to conclusion

that an unprecedented isomerisation, **4** → **6**, was being induced zirconium(IV) chloride.[5] Indeed, when **4** was treated with $ZrCl_4$ for 48 hours the methoxytetralin **6** was given in 67% yield, together with ~10% of **5** and recovered starting material.



Scheme 2

These results prompted us to investigate the isomerisation of 6-methoxytetralin **1** to 8-methoxytetralin **2**.[2] Exposure of **1** to 5 equivalents of zirconium(IV) chloride led to 53% conversion after 20 hours and an 83% conversion after 2 days (Scheme 1). Believing that the slow rate of isomerisation was due to the low solubility of zirconium(IV) chloride in chloroform, we examined the effects of solvent. In polar media (DMSO, DMF, ethanol, acetone and THF) the reaction either failed or gave unidentifiable side products. In non-polar solvents (dichloromethane, carbon tetrachloride, toluene, chloroform and pentane) rearrangement was facile but turnover was slow. Elevating the temperature proved deleterious, leading to product mixtures containing **1**, **2** and their demethylated analogues **17** and **18**.

Various Lewis acids were then examined. Aluminium trichloride, tin tetrachloride, iron trichloride, scandium triflate, antimony pentafluoride, yttrium trichloride, cadmium iodide, mercury(II) chloride, zinc iodide, copper(II) bromide and concentrated sulfuric acid failed to induce rearrangement; as did zirconocene dichloride, titanocene dichloride and zirconium(IV) fluoride. All the group IV metal tetrachlorides and tetrabromides studied gave the reaction as indicated in Table 1. In general, the bromides were superior to the chlorides and the zirconium and hafnium salts were superior to titanium tetrachloride.

Modest rate enhancements were noted when 1 molar equivalent of diethylamine or ethanethiol were added to the reaction mixture. In the latter case, demethylation of **2** to **18** occurred to a small extent. More notable was the realisation of near quantitative yields when reactions were conducted in the presence of phase transfer catalysts, crown ethers and lithium chloride (Table 2).

Table 1: The Rearrangement of **1** Induced by Group VI Metal Halides

Lewis Acid (5 equiv.)	time (h)	**2** %	**18** %
$TiCl_4$	170	51	-
$TiCp_2Cl_2$	48	-	-
ZrF_4	48	-	-
$ZrCl_4$	20	53	-
$ZrCl_4$	48	84	trace
$ZrCp_2Cl_2$	48	-	-
$ZrBr_4$	16	88	trace
$HfCl_4$	48	50	-
$HfBr_4$	28	50	19

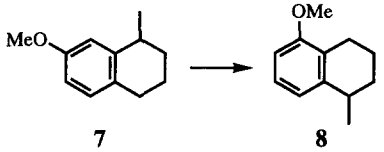
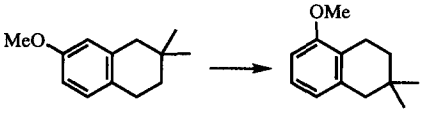
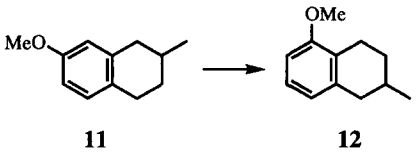
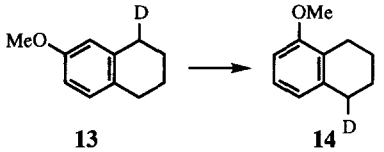
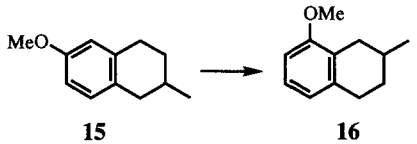
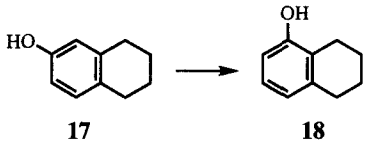
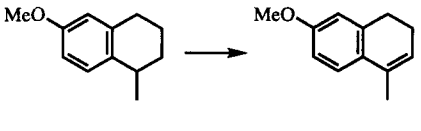
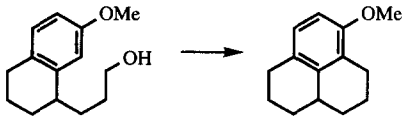
Table 2: The Effect of Additives on the $ZrCl_4$ Mediated Rearrangement of **1**

Additive	molar equiv.	time (h)	**2** %	**18** %
Et_2NH	1	120	94	-
EtSH	1	20	68	23
EtOH	1	48	-	-
LiCl	5	16	90	trace
Bu_4NBr	0.5	16	93	-
Bu_4NBF_4	0.5	16	91	-
Adogen® 464	0.5	16	85	-
Aliquat® 336	0.5	16	88	-
18-Crown-6	0.5	24	94	-

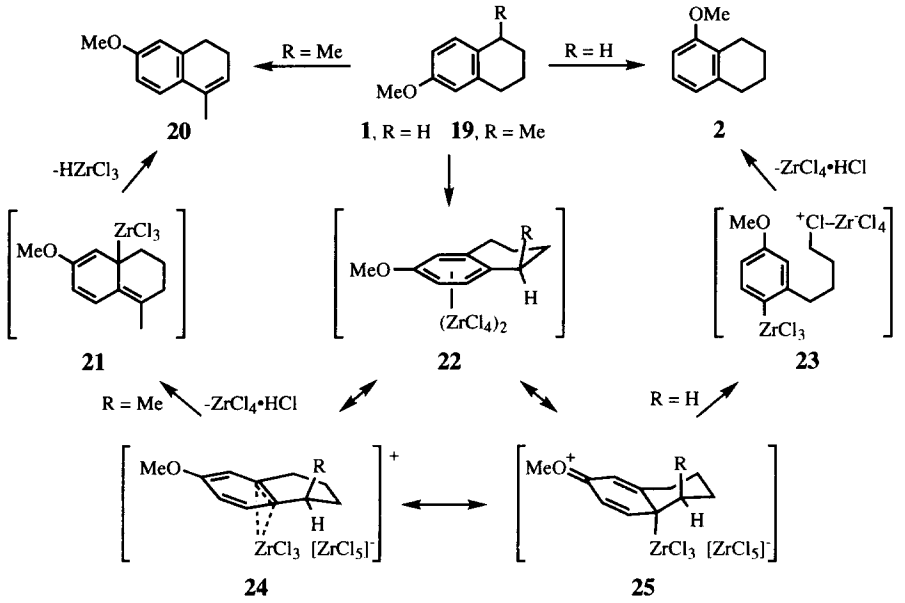
The advantages gained by using additives were undermined by the needed to use chromatographic purification to effect their removal from the product mixture. Through the simple expedient of conducting reactions in an ultrasound cleaning bath, complete isomerisation of **1** to **2** could be achieved within 1 hour and the product attained in a high state of purity (>98%) after aqueous work up (yield 95%).[6]

To delineate the scope and limitations of the reaction, a series of substituted 6-methoxytetralins were prepared, as detailed in the experimental section. With one exception (Table 3, Entry G), each was transformed into the corresponding 8-methoxytetralin on exposure to zirconium(IV) chloride (Table 3).[2] Most notably, rearrangement of 4-deutero-6-methoxytetralin **13** gave 4-deutero-8-methoxytetralin **14** exclusively (Entry D). In every case, substantial improvements in efficiency were realised under sonication. For example, rearrangement of 6-methoxy-3,3-dimethyltetralin **9** to 8-methoxy-3,3-dimethyltetralin **10** could be accomplished in 90% yield after 16 hours of ultrasonic irradiation compared to <10% conversion after 8 days for the silent reaction (Entry B).

Table 3: Further Examples of the Zirconium(IV) Chloride mediated Sliding Cyclohexane Rearrangement.

A  **7** **8**	CH_2Cl_2, r.t., 68%, 120 h. *With*))), 85%, 13 h.	**B**  **9** **10**	CH_2Cl_2, r.t., <10%, 200 h. *With*))), 90%, 16 h.
C  **11** **12**	CH_2Cl_2, r.t., 54%, 170 h. *With*))), 71%, 12 h.	**D**  **13** **14**	CH_2Cl_2, r.t., 62%, 48 h. *With*))), 81%, 3 h.
E  **15** **16**	CH_2Cl_2, r.t., 71%, 200 h. *With*))), 75%, 8 h.	**F**  **17** **18**	CH_2Cl_2, r.t., 38%, 20 h. *With*))), 74%, 8 h.
G  **19** **20**	CH_2Cl_2, r.t., 40%, 100 h. *With*))), 66%, 8 h.	**H**  **5** **6**	CH_2Cl_2, r.t., 10%, 48 h. *With*))), 65%, 12h.

Our postulate for the mechanistic course of the rearrangement is outlined in Scheme 3. We have assumed that, like durene,[7] 6-methoxytetralins forms 1:2 η^6-arene complex with zirconium(IV) chloride and that these exist as a hybrid between the three extreme resonance forms **22**, **24** and **25**. When steric encumbrance at C-1 is low (R = H), collapse *via* a retro-Friedel-Crafts alkylation to **23** occurs. An aromatic Friedel-Crafts alkylation and hydrolytic work up then gives the corresponding 8-methoxytetralin. However, when steric encumbrance at C-1 is high (R = Me), scission of the saturated ring is slowed and collapse of the arene complex proceeds by dehydrohalogenation to **21** and dehydrozirconation to **20**. That increasing the solubility of the reagent leads to rate enhancement, while substituents on the saturated ring suppress the reaction suggests that formation of the arene complex is rate limiting.



Scheme 3

In conclusion, we have shown that 6-methoxytetralins may be isomerised to 8-methoxytetralin through the action of zirconium(IV) chloride. The reaction proceeds *via* scission of the C-1 to C-8a bond and cyclisation by intramolecular Friedel-Crafts alkylation. Yields are good though turnover is slow. Rearrangements may be conducted in most non-polar solvents and are promoted by ultrasonic irradiation, phase transfer catalysts, crown ethers and lithium chloride. The reaction is also given by zirconium(IV) bromide, hafnium(IV) chloride and hafnium(IV) bromide.

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EXPERIMENTAL SECTION

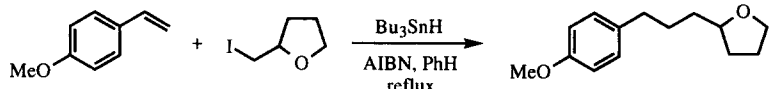
GENERAL REMARKS

Melting points were obtained using a Mel-Temp (II) apparatus and are uncorrected. UV spectra were recorded on a Pye Unicam SP800 spectrometer. Maxima and inflections (inf) are reported as λ_{max} followed in parentheses by the extinction coefficient ε ($dm^3mol^{-1}cm^{-1}$). IR spectra were recorded on a Perkin Elmer 1600 series Fourier transform infrared spectrometer using NaCl cells. Maxima are reported as ν_{max} followed by the signal intensity (described using the abbreviations s, strong; m, medium; w, weak; v, very; br, broad). ^1H n.m.r. spectra were recorded on a Bruker AC300 (300 MHz) or a Bruker AM360 (360 MHz) spectrometer. Chemical shifts (δ_H) are reported as values in parts per million relative to tetramethylsilane (δ 0.00) or residual $CHCl_3$ (δ 7.27). Multiplicities are described using the abbreviations s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; app., apparent. COSY experiments were performed on a Brucker AC300. N.O.e. experiments were performed on a Bruker AM360 spectrometer. ^{13}C spectra were recorded on a Bruker AC300 (75 MHz) spectrometer. Chemical shifts (δ_C) are reported as values in parts per million relative to tetramethylsilane (δ 0.00) or residual $CHCl_3$ (δ 77.2). Multiplicities refer to the signals in the off-resonance spectra, as determined by DEPT 135° and DEPT 90° experiments, and are described using the abbreviations s, singlet; d, doublet; t, triplet; q, quartet. Mass spectra were recorded on a variety of instruments. Signals are reported as values in atomic mass units and are followed in parentheses by the peak intensity relative to the base peak (100%).

All reactions were conducted under a nitrogen atmosphere using flame dried glassware. Magnetic stirring was used for all reaction except those involving sonication. Sonicated experiments were performed by partial immersion of the reaction vessel into the water filled bath of Branson 1200, Bransonic® ultrasound cleaner. Reactions were monitored by thin layer chromatography, using Macherey-Nagel Alugram Sil G/UV_{254} precoated aluminium foil plates of layer thickness 0.25mm (CAUTION: always switch off ultrasonic devices prior to tlc analysis). Compounds were visualised firstly by UV irradiation, then by exposure to iodine vapour and finally by heating plates exposed to solutions of potassium permanganate in aq. sodium carbonate or phosphomolybdic acid in ethanol. Column chromatography was performed on Sorbsil 60 silica (230-400 mesh), slurry packed and run under low pressure. THF was dried and deoxygenated by refluxing over sodium wire using benzophenone ketyl as indicator. All reagents used were used as supplied.

PREPARATION OF STARTING MATERIALS

2-(3-(4-Methoxyphenyl)-prop-1-yl)-tetrahydrofuran **3**

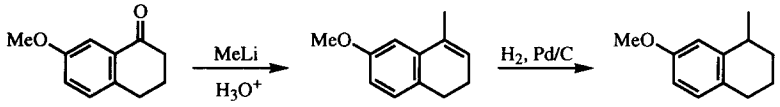


26 **27** **3**

To a stirred solution of 2-(iodomethyl)-tetrahydrofuran **27** (1.06 g, 5.00 mmol) and 4-methoxystyrene **26** (2.00 g, 14.9 mmol) in dry, degassed benzene (150 mL) were added Bu_3SnH (1.73 mL, 1.87 g, 6.42 mmol) and AIBN (20 mg, 0.12 mmol). The reaction was refluxed for 28 h then cooled to room temperature. Aqueous KF (6 M, 150 mL) was added and the biphasic mixture was stirred vigorously for 20 h then separated. The aqueous layer was extracted with Et_2O (2 x 50 mL) and the combined organic layers were dried ($MgSO_4$), filtered and evaporated under reduced pressure. Purification of the residue by chromatography (gradient elution, 1 - 30%

Et_2O in petrol) gave **3** (220 mg, 1.00 mmol, 20%) as a colourless oil; **IR** (neat) υ_{max} 2935 (s), 2850 (m), 1610 (m), 1580 (w), 1515 (s), 1465 (w), 1245 (s), 1175 (m), 1070 (m), 1035 (m), 830 (w) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 283 (2670), 275 (3220), 226 (7700) nm; **^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 7.11 (2H, d, J = 8.5 Hz, 2 x Ar*H*), 6.82 (2H, d, J = 8.5 Hz, 2 x Ar*H*), 3.86 (1H, dd, J = 14.1, 7.3 Hz, OC*H*H), 3.80 (3H, s, OCH_3), 3.80 (1H, obscured, OC*H*), 3.73 (1H, dd, J = 14.1, 6.6 Hz, OCH*H*), 2.90 (2H, t, J = 7.4 Hz, $ArCH_2$), 2.03 - 1.39 (8H, m) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ_C 157.8 (s), 134.7 (s), 129.4 (2 x d) 113.8 (2 x d), 79.4 (d), 67.8 (t), 55.4 (q), 35.4 (t), 35.2 (t), 31.5 (t), 28.6 (t), 25.9 (t) ppm; **HRMS** (EI) $[M]^+$ found: 220.1463, $C_{14}H_{20}O_2$ requires 220.1463; **LRMS** (EI) 220 (19%, $[M]^+$), 134 (100%, $[p\text{-}MeOC_6H_4CH_2CH_2\text{-}H]^+$), 121 (59%, $[p\text{-}MeOC_6H_4CH_2]^+$), 71 (20%).

7-Methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene **7**

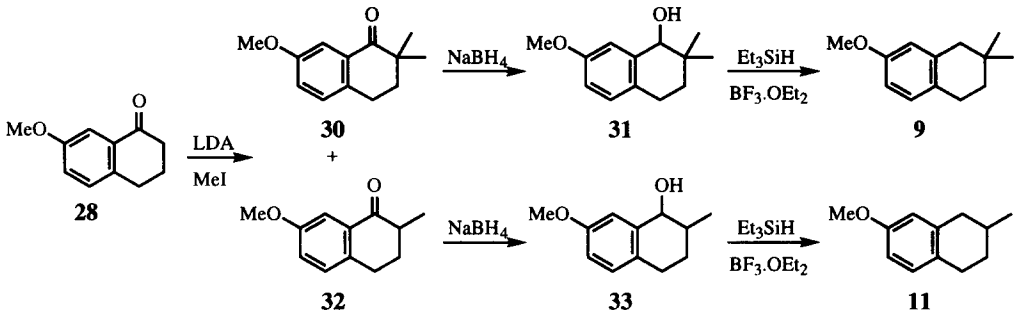


28 **29** **7**

To a cooled (-70°C) solution of 7-methoxy-1-tetralone **28** (1.30 g, 7.4 mmol) in THF (60 mL) was added MeLi•LiBr (6.0 mL, 1.5 M in Et_2O, 9.0 mmol). The reaction was warmed to room temperature then stirred for 16h, poured into 2M HCl (100 mL) and extracted with Et_2O (3 x 30 mL). The combined organic phases were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (neat petrol) gave 6-methoxy-4-methyl-1,2-dihydronaphthalene (1.14 g, 6.6 mmol, 89%) **29** as a colourless oil;[8] **IR** (neat) υ_{max} 2935 (s), 2830 (m), 1604 (s), 1570 (s), 1490 (s), 1455 (m), 1275 (s), 1260 (s), 1171 (s), 1045 (s), 870 (m), 800 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 302 (1600), 287 (2220), 256 (3200), 238 (4000) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.09 (1H, dt, J = 8.1, 1.0 Hz, ArH), 6.87 (1H, d, J = 2.7 Hz, ArH), 6.74 (1H, dd, J = 8.1, 2.7 Hz, ArH), 5.93 (1H, tq, J = 4.5, 1.6 Hz, =C*H*), 3.95 (3H, s, OCH_3), 2.74 (2H, t, J = 8.0 Hz, $ArCH_2$), 2.33 - 2.23 (2H, m, $ArCH_2CH_2$), 2.09 (3H, q, J = 1.6 Hz, CCH_3); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 158.5 (s), 137.1 (s), 132.3 (s), 128.7 (s), 128.0 (d), 126.3 (d), 111.0 (d), 109.8 (d), 55.5 (q), 27.6 (t), 23.7 (t), 19.5 (q); **LRMS** (EI), 175 (20%), 174 (98%, $[M]^+$), 160 (21%), 159 (100%, $[M\text{-}Me]^+$), 158 (40%), 144 (70%), 128 (45%), 115 (60%).

A vigorously stirred solution of 6-methoxy-4-methyl-1,2-dihydronaphthalene **29** (394 mg, 2.26 mmol) and 5% Pd-C (221 mg, 0.10 mmol) in EtOAc (14 mL) was purged three times with N_2 and three times with H_2 before being stirred under a H_2 atmosphere for 18 h. The reaction mixture was then purged with N_2 for 20 min, filtered through celite and evaporated at reduced pressure. Column chromatography (neat petrol) gave 7-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene **7** (286 mg, 1.63 mmol, 71%) as a pale yellow oil;[9,10] **IR** (neat) υ_{max} 2995 (m), 2930 (s), 2860 (s), 2895 (m), 1615 (s), 1575 (s), 1500 (s), 1465 (s), 1250 (s), 1150 (s), 1130 (m), 1045 (s), 800 (s), 700 (m), cm^{-1}; **UV** (MeOH) λ_{max} (ε) 277 (2600), 231 (5460) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.06 (1H, d, J = 8.5 Hz, Ar*H*), 6.85 (1H, d, J = 2.8 Hz, Ar*H*), 6.77 (1H, dd, J = 8.5, 2.8 Hz, Ar*H*), 3.87 (3H, s, OCH_3), 2.97 (1H, app sextet, J = 6.5 Hz, ArC*H*), 2.87 - 2.73 (2H, m, $ArCH_2$), 2.06 - 1.87 (2H, m, $ArCH_2CHHCHH$), 1.85 - 1.73 (1H, m, ArCHCH*H*), 1.64 - 1.53 (1H, m, $ArCH_2CHH$), 1.38 (3H, d, J = 7.0 Hz, $CHCH_3$); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.8 (s), 143.5 (s), 130.0 (d), 129.2 (s), 113.4 (d), 111.6 (d), 55.4 (q), 33.0 (d), 31.7 (t), 29.4 (t), 23.1 (q), 20.9 (t); **HRMS** (EI) $[M]^+$ found: 176.1201; $C_{12}H_{16}O$ requires 176.1201; **LRMS** (EI) 177 (15%), 176 (90%, $[M]^+$), 161 (100%, $[M\text{-}Me]^+$), 148 (30%, $[M\text{-}CH_2CH_2]^+$), 134 (70%), 115 (30%), 91 (30%).

2,2-Dimethyl-7-methoxy-1,2,3,4-tetrahydronaphthalene **9** and
7-Methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **11**



To a cooled (0°C) solution of *i*-Pr_2NH (0.87 mL, 630 mg, 6.2 mmol) in THF (50 mL) was added BuLi (4.0 mL, 1.6 M in hexanes, 6.4 mmol). After 40 min the temperature was lowered (-75°C) and 6-methoxy-1-tetralone **28** (900 mg, 5.11 mmol) in THF (5 mL) added. The reaction was allowed to warm to 5°C over 4h, cooled to -20°C and MeI (0.64 mL, 1.46 g, 10.3 mmol) added. After 16 h the reaction was poured into water (50 mL) and extracted with Et_2O (3 x 40 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (20% Et_2O in petrol) gave firstly 2,2-dimethyl-7-methoxy-1-tetralone **30** (315 mg, 1.54 mmol, 30%) as a colourless oil;[11,12] **IR** (neat) υ_{max} 2955 (s), 2920 (s), 2850 (m), 1680 (s), 1610 (s), 1495 (s), 1460 (s), 1420 (m), 1325 (m), 1295 (m), 1260 (s), 1200 (m), 1160 (m), 1035 (s), 1000 (m), 870 (m), 825 (m), 780 (m), 730 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 317 (3060), 281 (3270), 243 (1120), 227 (1120) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.53 (1H, d, *J* = 2.6 Hz, Ar*H*), 7.14 (1H, d, *J* = 8.5 Hz, Ar*H*), 7.05 (1H, dd, 8.5, 2.6 Hz, Ar*H*), 3.84 (3H, OCH_3), 2.92 (2H, t, *J* = 6.3 Hz, $ArCH_2$), 1.97 (2H, t, *J* = 6.3 Hz, $ArCH_2CH_2$), 1.22 (6H, s, $C(CH_3)_2$); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 203.0 (s), 158.5 (s), 136.1 (s), 132.3 (s), 130.0 (d), 121.6 (d), 109.9 (d), 55.6 (q), 41.6 (s), 37.0 (t), 25.0 (t), 24.5 (2 x q); **LRMS** (ES) 205 (70%, $[MH]^+$), 204 (20%, $[M]^+$), 191 (100%), 190 (10%), 151 (30%); then 7-methoxy-2-methyl-1-tetralone **32** (282 mg, 1.48 mmol, 29%);[13] a colourless oil; **IR** (neat) υ_{max} 3050 (w), 2930 (s), 2869 (s), 1680 (s), 1610 (s), 1495 (s), 1450 (s), 1325 (s), 1275 (s), 1200 (m), 1035 (s), 995 (m), 875 (m), 820 (m), 730 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 315 (1625), 279 (1540), 245 (3780), 232 (2170) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.52 (1H, d, *J* = 2.9 Hz, Ar*H*), 7.15 (1H, d, *J* = 8.5 Hz, Ar*H*), 7.04 (1H, dd, *J* = 8.5, 2.9 Hz, Ar*H*), 3.85 (3H, s, OCH_3), 2.98 (1H, dddd, *J* = 16.1, 10.3, 4.4, 0.7 Hz, ArC*H*H), 2.90 (1H, ddd, *J* = 16.1, 5.5, 4.4 Hz, ArCH*H*), 2.57 (1H, dqd, *J* = 11.8, 7.0, 4.4 Hz, $CHCH_3$), 2.19 (1H, app dq, *J* = 13.2, 4.4 Hz, CHC*H*), 1.86 (1H, dddd, *J* = 13.2, 11.8, 10.3, 5.5 Hz, CHCH*H*), 1.14 (3H, d, *J* = 7.0 Hz, $CHCH_3$); **^{1}C NMR** δ_C (75 MHz, $CDCl_3$) 200.9 (s), 158.4 (s), 137.0 (s), 133.3 (s), 130.1 (d), 121.6 (d), 109.4 (d), 55.6 (q), 42.6 (d), 31.7 (t), 28.1 (t), 15.6 (q); **LRMS** (ES) 191 (45%, $[MH]^+$), 124 (100%).

To a stirred solution of 2,2-dimethyl-7-methoxy-1-tetralone **30** (180 mg, 0.88 mmol) in MeOH (20 mL) was added $NaBH_4$ (70 mg, 1.85 mmol). After 2.5 h the reaction was poured into water (50 mL) and extracted with Et_2O (3 x 30 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (40% Et_2O in petrol) gave 2,2-dimethyl-1-hydroxy-7-methoxy-1,2,3,4-tetrahydronaphthalene **31** (162 mg, 0.79 mmol, 89%) as a colourless oil;[11] **IR** (neat) υ_{max} 3420 (br s), 2920 (s), 2860 (m), 1615 (m), 1580 (w), 1500 (s), 1460 (m), 1265 (s), 1155 (m), 1110 (m), 1040 (s), 855 (m), 815 (m), 720

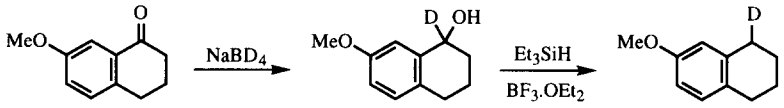
(m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 287 (1250), 281 (1330), 234 (1150) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.04 - 7.00 (2H, m, 2 x Ar*H*), 6.78 (1H, dd, *J* = 8.5, 2.5 Hz, Ar*H*), 4.22 (1H, s, ArC*H*OH), 3.80 (3H, s, OCH_3), 2.76 (1H, app dt, *J* = 17.3, 6.7 Hz ArC*H*H), 2.69 (1H, app dt, *J* = 17.3, 6.7, ArCH*H*), 1.93 (1H, br s, O*H*), 1.79 (1H, dt, *J* = 13.5, 6.7 Hz, $ArCH_2CHH$), 1.54 (1H, dt, *J* = 13.5, 6.8 Hz, $ArCH_2CHH$), 1.00 (3H, s, CCH_3), 0.99 (3H, s, CCH_3); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 158.1 (s), 139.8 (s), 129.8 (d), 128.0 (s), 114.1 (d), 113.1 (d), 77.0 (d), 55.4 (q), 34.0 (s), 32.6 (t), 26.0 (q), 25.3 (t), 22.3 (q); **LRMS** (EI) 206 (45%, $[M]^+$), 188 (13%, $[M-H_2O]^+$), 173 (17%), 150 (100%), 121 (31%).

To a cooled (-60°C) solution of 2,2-dimethyl-1-hydroxy-7-methoxy1,2,3,4-tetrahydronaphthalene **31** (150 mg, 0.73 mmol) in dichloromethane (4 mL) were added Et_3SiH (0.35 mL, 255 mg, 2.19 mmol) and $BF_3.Et_2O$ (0.18 mL, 0.20 g, 1.42 mmol). The reaction was warmed to -10°C over 4 h before the addition of saturated K_2CO_3 (10 mL), and extraction with dichloromethane (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (gradient elution, 0 - 10% Et_2O in petrol) gave 2,2-dimethyl-7-methoxy-1,2,3,4-tetrahydronaphthalene **9** (122 mg, 0.64 mmol, 88%) as a colourless oil;[11] **IR** (neat) υ_{max} 2995 (w), 2950 (s), 2910 (s), 2840 (m), 1610 (m), 1500 (s), 1460 (s), 1270 (m), 1245 (m), 1155 (m), 1045 (m), 840 (m), 805 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 286 (4240), 279 (4500), 234 (4690) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.03 (1H, d, *J* = 8.5 Hz, Ar*H*), 6.71 (1H, dd, *J* = 8.5, 2.8 Hz, Ar*H*), 6.60 (1H, d, *J* = 2.8 Hz, Ar*H*), 3.79 (3H, OCH_3), 2.75 (2H, t, *J* = 6.7 Hz, $ArCH_2CH_2$), 2.53 (2H, s, $ArCH_2C$), 1.57 (2H, t, *J* = 6.7 Hz, $ArCH_2CH_2$), 1.00 (6H, s, $C(CH_3)_2$); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.5 (s), 137.6 (s), 129.6 (d), 127.8 (s), 114.0 (d), 111.8 (d), 55.2 (q), 43.9 (t), 36.3 (t), 29.4 (s), 28.1 (2 x q), 25.7 (t); **LRMS** (EI) 190 (73%, $[M]^+$), 175 (14% $[M-Me]^+$), 134 (100%, $[M-C(CH_3)_2CH_2]^+$).

To a solution of 7-methoxy-2-methyl-1-tetralone **32** (180 mg, 0.95 mmol) in MeOH (10 mL) was added $NaBH_4$ (70 mg, 1.85 mmol). After 14 h the reaction was poured into 2M HCl (50 mL) and extracted with Et_2O (3 x 30 mL). The combined organic phases were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (50% Et_2O in petrol) gave 1-hydroxy-7-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **33** (132 mg, 0.69 mmol, 73%) as an inseparable, 2:1 mixture of diastereoisomers; a colourless oil;[14] **IR** (neat) υ_{max} 3370 (br s), 2925 (s), 2860 (w), 1610 (m), 1500 (s), 1460 (m), 1250 (m), 1160 (w), 1040 (m), 810 (w) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 288 (1580), 279 (1730), 230 (2820) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) major diastereoisomer; 7.09 (1H, d, *J* = 2.9 Hz, ArC*H*), 7.01 (1H, d, *J* = 8.5 Hz, Ar*H*), 6.77 (1H, dd, *J* = 8.5, 2.9 Hz, Ar*H*), 4.27 (1H, d, *J* = 8.3 Hz, ArC*H*OH), 3.80 (3H, s, OCH_3), 2.85 - 2.63 (2H, m, $ArCH_2$), 1.98 - 1.45 (4H, m, CH_2CHCHOH), 1.14 (3H, d, *J* = 6.6 Hz, CHCH_3), minor diastereoisomer; 7.05 (1H, d, *J* = 8.5 Hz, Ar*H*), 6.91 (1H, d, *J* = 2.9 Hz, Ar*H*), 6.81 (1H, dd, *J* = 8.5, 2.9 Hz, Ar*H*), 4.52 (1H, d, *J* = 3.3 Hz, ArC*H*OH), 3.80 (3H, s, OCH_3), 2.85 - 2.63 (2H, m, $ArCH_2$), 1.98 - 1.45 (4H, m, CH_2CHCHO*H*), 1.13 (3H, d, *J* = 7.0 Hz, CHCH_3); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) major diastereoisomer 158.2 (s) 140.3 (s), 130.1 (s), 129.7 (d), 114.0 (d), 112.2 (d), 75.4 (d), 55.6 (q), 37.5 (d), 28.8 (t), 27.5 (t), 18.5 (q), minor diastereoisomer 157.9 (s), 139.8 (s), 128.9 (d), 128.8 (s), 114.7 (d), 114.0 (d), 71.9 (d), 55.6 (d), 34.4 (d), 28.1 (t), 25.2 (t), 16.9 (q); **LRMS** (APCI) 192 (13%, $[M]^+$), 191 (10%, $[M-H]^+$), 175 (100%, $[MH-H_2O]^+$), 174 (22%, $[M-H_2O]^+$).

To a cooled (-40°C) solution of 1-hydroxy-7-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **33** (230 mg, 1.20 mmol) in dichloromethane (4.5 mL) were added Et_3SiH (0.48 mL, 0.35 g, 3.0 mmol) and $BF_3.Et_2O$ (0.37 mL, 0.41 g, 2.9 mmol). The reaction was warmed to 0°C over 90 min, stirred for a further 3 h then saturated K_2CO_3 (2 mL) was added. The resulting solution was extracted with dichloromethane (3 x 5 mL), and the combined organic phases were dried ($MgSO_4$), filtered and evaporated at reduced pressure. Column chromatography (gradient elution, 0 - 3% Et_2O in petrol) gave 7-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **11** (160 mg, 0.91 mmol, 76%) as a colourless oil;[9] **IR** (neat) υ_{max} 3000 (w), 2920 (s), 2835 (w), 1635 (m), 1610 (s), 1585 (m), 1500 (s), 1470 (s), 1260 (s), 1215 (s), 1160 (m), 1105 (m), 1040 (s), 840 (m), 765 (w) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 265 (2900), 230 (5030) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.02 (1H, d, *J* = 8.4 Hz, Ar*H*), 6.71 (1H, dd, *J* = 8.4, 2.9 Hz, Ar*H*), 6.63 (1H, d, *J* = 2.9 Hz, Ar*H*), 3.73 (3H, s, OCH_3), 2.86 - 2.74 (3H, m, ArC*H* + ArCH_2), 2.41 (1H, app ddquin, *J* = 16.5, 10.6, 1.1 Hz, ArCH*H*CH), 1.95 - 1.77 (2H, m, $ArCH_2CHHCH$), 1.39 (1H, m, $ArCH_2CHH$), 1.08 (3H, d, *J* = 6.5 Hz, $CHCH_3$); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.6 (s), 138.8 (s), 129.8 (d), 129.0 (s), 113.8 (d), 111.9 (d), 55.4 (q), 38.6 (t), 31.9 (t), 29.4 (d), 28.6 (t), 22.1 (q); **HRMS** (EI) $[M]^+$ found: 176.1201; $C_{12}H_{16}O$ requires 176.1196; **LRMS** (EI), 176 (85%, $[M]^+$), 161 (20%, $[M-Me]^+$), 159 (25%), 134 (100%, $[M-CH_2CHCH_3]^+$), 91 (20%).

1-Deutero-7-methoxy-1,2,3,4-tetrahydronaphthalene **13**



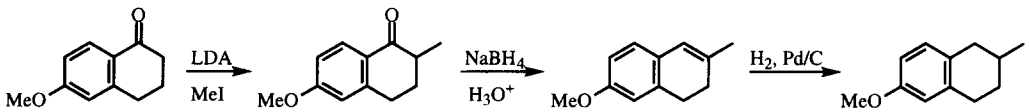
34 **35** **13**

To a solution of 7-methoxy-1-tetralone **34** (600 mg, 3.41 mmol) in methanol (20 mL) was added sodium borodeuteride (143 mg, 3.41 mmol). After 90 min, the reaction mixture was poured into water (120 mL) and extracted with ether (3 x 60 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated at reduced pressure to give 1-deutero-1-hydroxy-7-methoxy-1,2,3,4-tetrahydronaphthalene **35** (591 mg, 3.30 mmol, 97%) as a pale yellow oil; **IR** (neat) υ_{max} 3395 (br s), 2910 (s), 2840 (s), 2125 (m), 1880 (w), 1610 (s), 1500 (m), 1445 (m) cm^{-1}; **UV** (MeOH) λ_{max} (e) 288 (1700), 281 (1800), 233 (1600) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.02 (1H, d, *J* = 8.5 Hz, Ar*H*), 6.99 (1H, d, *J* = 2.6 Hz, Ar*H*), 6.78 (1H, dd, *J* = 8.5, 2.6 Hz, Ar*H*), 3.80 (3H, s, OCH_3), 2.82 - 2.60 (2H, m, ArCH_2), 2.08 - 1.70 (5H, m, CH_2CH_2CDOH); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 158.1 (s), 139.9 (s), 130.1 (d), 129.3 (s), 114.5 (d), 112.8 (d), 68.2 (1:1:1 t, J_{CD} = 22.0 Hz), 55.5 (q), 32.4 (t), 28.6 (t), 19.3 (t); **HRMS** (EI), found: $[M]^+$, 179.1057; $C_{11}H_{13}O_2D$ requires 179.1057; **LRMS** (EI) 179 (18%, $[M]^+$), 161 (50%, $[M-H_2O]^+$), 151 (15%, $[M-CH_2CH_2]^+$), 146 (30%), 130 (40%), 121 (80%), 116 (100%).

To a cooled (-50°C) solution of 1-deutero-1-hydroxy-7-methoxy-1,2,3,4-tetrahydronaphthalene **35** (650 mg, 3.63 mmol) in CH_2Cl_2 (15 mL) were added $BF_3.Et_2O$ (0.90 mL, 1.0 g, 7.1 mmol) and Et_3SiH (1.7 mL, 1.2 g, 10 mmol). The reaction was stirred at -15°C for 5 h then saturated K_2CO_3 solution (10 mL) was added. The mixture was partitioned, separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated at reduced pressure. Column chromatography (neat petrol) gave 1-deutero-7-methoxy-1,2,3,4-tetrahydronaphthalene **13** (367 mg, 2.25 mmol, 62%) as a pale yellow oil; **IR** υ_{max} 2995 (m), 2930 (s), 2860 (m), 2155 (w), 1610 (s), 1580 (w), 1500 (s), 1460 (m), 1255 (s), 1040 (s) cm^{-1}; **UV** λ_{max}

(ε) 287 (1800), 279 (2000), 230 (3100) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.08 (1H, d, J = 8.1 Hz, Ar*H*), 6.78 (1H, dd, J = 8.1, 2.6 Hz, Ar*H*), 6.72 (1H, d, J = 2.6 Hz, Ar*H*), 3.86 (3H, s, OCH_3), 2.87 - 2.77 (3H, m, $ArCH_2$ + Ar*CH*), 1.90 - 1.86 (4H, m, CH_2CH_2CH); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.5 (s), 138.1 (s), 130.0 (d), 129.3 (s), 113.8 (d), 111.9 (d), 55.3 (q), 29.5 (d of 1:1:1 t, J_{CD} = 19.1 Hz), 28.7 (t), 23.5 (t), 23.2 (t); **HRMS** (EI), found: $[M]^+$, 163.1110; $C_{11}H_{13}OD$ requires 163.1110; **LRMS** (EI) 163 (71%, $[M]^+$), 148 (35%, $[M\text{-}CH_3]^+$), 135 (75%, $[M\text{-}CH_2CH_2]^+$), 134 (76%), 92 (58%), 49 (100%).

6-Methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **15**



34 **36** **37** **15**

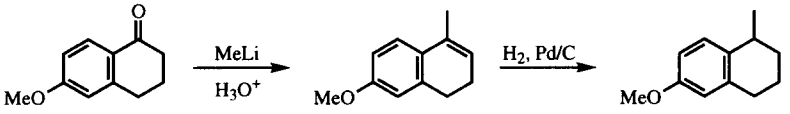
To a cooled (0°C) solution of *i*-Pr_2NH (0.87 mL, 630 mg, 6.2 mmol) in THF was added BuLi (4.1 mL, 1.5 M in hexanes, 6.15 mmol). After 40 min the temperature was lowered (-75°C) and 6-methoxy-1-tetralone **34** (900 mg, 5.11 mmol) in THF (5 mL) added. The reaction mixture was allowed to warm to 5°C over 4 h then cooled to -75°C and MeI (0.64 mL, 1.46 g, 10.3 mmol) added. After 16 h the reaction was poured into water (50 mL) and extracted with Et_2O (3 x 40 mL). The combined organic phases were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (10% Et_2O in petrol) gave 2-methyl-6-methoxy-1-tetralone **36** (884 mg, 4.60 mmol, 90%) as a colourless oil;[15] **IR** (neat) υ_{max} 2960 (w), 2930 (s), 2860 (w), 1675 (s), 1600 (s), 1495 (m), 1455 (m), 1360 (m), 1085 (m), 1030 (m), 970 (m), 760 (w) cm^{-1}; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 8.01 (1H, d, J = 8.7 Hz, Ar*H*), 6.82 (1H, dd, J = 8.7, 2.6 Hz, Ar*H*), 6.69 (1H, d with fine splitting, J = 2.6 Hz, Ar*H*), 3.85 (3H, OCH_3), 3.07 - 2.87 (2H, m, $ArCH_2$), 2.55 (1H, dqd, J = 11.8, 6.7, 4.8 Hz, $CHCH_3$), 2.18 (1H, dq, J = 13.2, 4.8 Hz, $ArCH_2CHH$), 1.87 (1H, dddd, J = 13.2, 11.8, 10.7, 5.2 Hz, $ArCH_2CHH$), 1.28 (3H, d, J = 6.7 Hz, $CHCH_3$); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 199.7 (s), 163.5 (s), 146.8 (s), 129.9 (d), 126.2 (s), 113.2 (d), 112.6 (d), 55.5 (q), 42.4 (d), 31.6 (t), 29.3 (t), 15.7 (q); **LRMS** (ES) 192 (15%), 191 (100%, $[MH]^+$), 142 (50%).

To a stirred solution of 2-methyl-6-methoxy-1-tetralone **36** (677 mg, 3.53 mmol) in MeOH (20 mL) was added $NaBH_4$ (270 mg, 7.14 mmol). After 90 min the reaction was poured into 2M HCl (30 mL) and extracted with Et_2O (3 x 50 mL). The combined organic phases were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (neat petrol) gave 7-methoxy-3-methyl-1,2-dihydronaphthalene **37** (207 mg, 1.19 mmol, 34%) as a colourless oil;[16] **IR** (neat) υ_{max} 3000 (w), 2920 (s), 2880 (m), 2830 (s), 1610 (s), 1595 (s), 1465 (m), 1430 (s), 1330 (m), 1295 (s), 1240 (s), 1155 (s), 1110 (m), 1100 (m), 1040 (s), 980 (w), 855 (s), 800 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 271 (3730), 230 (5550) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 6.93 (1H, dd, J = 7.0, 1.7 Hz, Ar*H*), 6.71 (2H, m, 2 x Ar*H*), 6.22 (1H, q, J = 1.5 Hz, =C*H*), 3.85 (3H, s, OCH_3), 2.84 (2H, app t, J = 8.3 Hz, $ArCH_2$), 2.26 (2H, app ddquin, J = 8.5, 7.8, 1.2 Hz, $=CCH_2$), 1.94 (3H, q, J = 1.2 Hz, CCH_3); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 158.2 (s), 135.9 (s), 135.6 (s), 128.8 (s), 126.1 (d), 113.8 (d), 112.8 (d), 111.2 (d), 55.4 (q), 28.8 (t), 28.7 (t), 23.6 (q); **LRMS** (ES) 174 (60%, $[M]^+$), 159 (55%, $[M\text{-}Me]^+$), 150 (100%), 137 (20%), 121 (20%).

A vigorously stirred solution of 7-methoxy-3-methyl-1,2-dihydronaphthalene **37** (150 mg, 0.86 mmol) and 5% Pd-C (221 mg, 0.10 mmol) in EtOAc (10 mL) was purged three times with N_2 and three times with H_2 then stirred under a H_2 atmosphere for 24 h. The reaction was then purged with N_2 for 25 min, filtered through celite and

evaporated at reduced pressure to give 6-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **15** (135 mg, 0.77 mmol, 89%) as a colourless oil;[17] **IR** (neat) υ_{max} 3000 (w), 2920 (s), 2835 (m), 1615 (s), 1500 (s), 1460 (m), 1270 (m), 1240 (m), 1160 (m), 1040 (m), 845 (m), 815 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 288 (1610), 279 (1850), 231 (3050) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.05 (1H, d, J = 8.3 Hz, Ar*H*), 6.76 (1H, dd, J = 8.3, 2.8 Hz, Ar*H*), 6.71 (1H, d, J = 2.8 Hz, Ar*H*), 3.89 (3H, s, OCH_3), 2.88 (2H, 4 intense lines, second order A_2MX or ABMX, $ArCH_2$), 2.85 (1H, dd with fine splitting, J = 16.0, 4.9 Hz, ArC*H*H), 2.40 (1H, dd with fine splitting, J = 16.0, 10.7 Hz, ArCH*H*), 1.99 - 1.82 (2H, m, $ArCH_2CHCHH$), 1.45 (1H, ddt, J = 13.6, 11.0, 8.4, $ArCH_2HH$), 1.14 (3H, d, J = 6.4 Hz, $CHCH_3$); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.6 (s), 137.9 (s), 130.0 (d), 129.3 (s), 113.6 (d), 111.9 (d), 55.4 (q), 37.5 (t), 29.8 (t), 29.7 (t), 29.7 (d), 22.1 (q); **LRMS** (EI) 176 (100%, $[M]^+$), 161 (40%, $[M-Me]^+$), 145 (25%, $[M-MeOH]^+$), 134 (85%, $[M-CH_2CHCH_3]^+$), 121 (20%), 115 (25%), 91 (50%).

6-Methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene **19**



34 **20** **19**

To a cooled (-70°C) solution of 6-methoxy-1-tetralone **34** (1.30 g, 7.39 mmol) in THF (60 mL) was added MeLi•LiBr (6 mL, 1.5M in hexanes, 9.0 mmol). The reaction was warmed to room temperature, stirred for 48 h then poured into water (50 mL) and extracted with Et_2O (2 x 50 mL) and EtOAc (50 mL). The combined organic phases were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (gradient elution, 1 - 80% Et_2O in petrol) gave 4-methyl-7-methoxy-1,2-dihydronaphthalene **20** (908 mg, 5.22 mmol, 71%) as a colourless oil;[8,17,18] **IR** (neat) υ_{max} 3040 (w), 2935 (s), 2883 (s), 1510 (s), 1500 (s), 1465 (s), 1430 (s), 1380 (s), 1300 (s), 1250 (s), 1140 (s), 1075 (s), 1040 (s), 825 (s), 675 (s) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 269 (7240), 223 (6620) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.17 (1H, d, J = 8.3 Hz, Ar*H*), 6.77 (1H, dd, J = 8.3, 2.9 Hz, Ar*H*), 6.76 (1H, d, J = 2.9 Hz, Ar*H*), 5.75 (1H, tq, J = 4.4, 1.5 Hz, =C*H*), 3.88 (3H, s, OCH_3), 2.77 (2H, t, J = 8.0 Hz, $ArCH_2$), 2.26 (2H, m, $ArCH_2CH_2$), 2.05 (3H, q, J = 1.5 Hz, CCH_3); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 158.6 (s), 138.3 (s), 132.0 (s), 129.3 (s), 124.1 (d), 123.1 (d), 113.8 (d), 111.0 (d), 55.5 (q), 29.1 (t), 23.4 (t), 19.6 (q); **LRMS** (EI), 175 (20%), 174 (60%, M^+), 173 (35%), 160 (30%), 159 (100%, $[M-Me]^+$), 144 (55%), 115 (55%).

A vigorously stirred solution of 4-methyl-7-methoxy-1,2-dihydronaphthalene **20** (393 mg, 2.26 mmol) and 5% Pd-C (221 mg, 0.10 mmol) in EtOAc (14 mL) was purged three times with N_2 and three times with H_2 then stirred under a H_2 atmosphere for 18h. The reaction mixture was then purged with N_2 for 30 min, filtered through celite and evaporated at reduced pressure to give 6-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene **19** (320 mg, 1.82 mmol, 80%) as a pale yellow oil;[10,16] **IR** (neat) υ_{max} 3060 (w), 2925 (s), 2835 (m), 1610 (s), 1580 (m), 1500 (s), 1465 (m), 1370 (m), 1255 (s), 1155 (m), 1045 (s), 870 (m), 830 (m), 815 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 287 (2520), 278 (2730), 237 (4250) nm; **^{1}H NMR** δ_{max} (300 MHz, $CDCl_3$) 7.16 (1H, d, J = 8.5 Hz, Ar*H*), 6.75 (1H, dd, J = 8.5, 2.8 Hz, Ar*H*), 6.64 (1H, d, J = 2.8 Hz, Ar*H*), 3.81 (3H, s, OCH_3), 2.88 (1H, app quin, J = 7.0 Hz, $CHCH_3$), 2.77 (2H, m, $ArCH_2$), 2.01 - 1.80 (2H, m, ArCHC*H*HC*H*H), 1.77 (1H, m, $ArCH_2CHH$), 1.56 (1H, m, ArCHCH*H*), 1.30 (3H, d, J = 7.0 Hz, $CHCH_3$); **^{1}H-^{1}H COSY** was used to establish the assignments given above; **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.5 (s), 138.2 (s), 134.6 (s), 129.2 (d), 113.6 (d), 112.2 (d), 55.4 (q), 32.0 (d), 32.0 (t), 30.6 (t), 23.2 (q), 20.7 (t); **HRMS** (EI) $[M]^+$ found: 176.1187; $C_{12}H_{16}O$ requires 176.1201; **LRMS** (EI), 177 (20%), 176 (90%, M^+), 161 (100%, $[M-Me]^+$), 146 (50%), 144 (70%, $[M-MeOH]^+$), 115 (65%), 91 (60%).

GENERAL PROCEDURES FOR EFFECTING THE SLIDING CYCLOHEXANE REARRANGEMENT

Method A - The Silent Reaction

To a solution of 6-methoxy-1,2,3,4-tetrahydronaphthalene **1** (500 mg, 3.09 mmol) in chloroform (100 mL) was added $ZrCl_4$ (3.50 g, 15.0 mmol). After 40 h the red solution was poured into ice water (150 mL) and extracted with dichloromethane (3 x 30 mL). The combined organic phases were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (neat petrol) gave 5-methoxy-1,2,3,4-tetrahydronaphthalene **2** (420 mg, 2.59 mmol, 84%).

Method B - The Ultrasound Promoted Reaction

To a solution of 6-methoxy-1,2,3,4-tetrahydronaphthalene **1** (75 mg, 0.46 mmol) in dichloromethane (5 mL) was added $ZrCl_4$ (535 mg, 2.30 mmol). The reaction was subjected to ultrasonic irradiation for 1 h then poured into water (20 mL) and extracted with dichloromethane (2 x 10 mL). The combined organic phases were dried ($MgSO_4$), evaporated at reduced pressure and eluted with petrol through a plug of silica to give 5-methoxy-1,2,3,4-tetrahydronaphthalene **2** (69 mg, 0.43 mmol, 92%).

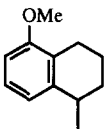
Method C :- Representative Example of the Use of Additives

To a solution of 6-methoxy-1,2,3,4-tetrahydronaphthalene **1** (150 mg, 0.93 mmol) in dichloromethane (10 mL) were added $ZrCl_4$ (1.07 g, 4.59 mmol) and LiCl (200 mg, 4.72 mmol) in single portions. After 16 h the reaction was poured into water (50 mL) and extracted with dichloromethane (2 x 50 mL). The combined organic phases were dried ($MgSO_4$), filtered and evaporated at reduced pressure. Column chromatography (neat petrol) gave 5-methoxy-1,2,3,4-tetrahydronaphthalene **2** (135 mg, 0.83 mmol, 90%).

Data obtained for 5-methoxy-1,2,3,4-tetrahydronaphthalene: a colourless oil; **IR** (neat) υ_{max} 3065 (w), 3000 (w), 2930 (s), 2835 (m), 1605 (m), 1585 (s), 1505 (m), 1470 (m), 1335 (m), 1310 (m), 1255 (s), 1095 (s), 825 (m), 765 (s) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 277 (1740), 260 (1730), 232 (2440) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.10 (1H, dd, J = 8.1, 7.0 Hz, Ar*H*), 6.77 (1H, d, J = 7.0 Hz, Ar*H*), 6.71 (1H, d, J = 8.1 Hz, Ar*H*), 3.84 (3H, s, OCH_3), 2.82 (2H, t, J = 5.5 Hz, $ArCH_2$), 2.72 (2H, app dd, J = 6.3, 5.1 Hz, $ArCH_2$), 1.84 (4H, m, $ArCH_2CH_2CH_2$); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.6 (s), 138.7 (s), 126.1 (s), 125.9 (d), 121.6 (d), 106.9 (d), 55.4 (q), 29.9 (t), 23.3 (t), 23.1 (2 x t) were consistent with literature reports.[19]

COMPOUNDS PREPARED BY ANALOGOUS PROCEDURES

5-Methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene **8**



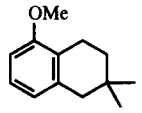
Method A :- 7-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene **7** (128 mg, 0.73 mmol), chloroform (5 mL), $ZrCl_4$ (850 mg, 3.65 mmol), 7 days, gave **8** (87 mg, 0.49 mmol, 68%).

Method B :- 7-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene **7** (94 mg, 0.53 mmol), dichloromethane (5 mL), $ZrCl_4$ (622 mg, 2.67 mmol), 13 h, gave **8** (80 mg, 0.45 mmol, 85%).

Method C :- 7-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene **7** (50 mg, 0.28 mmol), CH_2Cl_2 (5 mL), $ZrCl_4$ (535 mg, 2.3 mmol), LiCl (60 mg, 1.42 mmol), 18-crown-6 (80 mg),))), 2 h, gave **8** (38 mg, 0.22 mmol, 76%).
Data: A yellow oil;[20] **IR** (neat) υ_{max} 2930 (s), 2865 (m), 1585 (m), 1460 (s), 1440 (w), 1250 (s), 1100 (w), 1070 (m), 1040 (w), 775 (m), 720 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 277 (580), 270 (580), 227 (1660) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.13 (1H, t, J = 7.9 Hz, Ar*H*), 6.86 (1H, d, J = 7.9 Hz, Ar*H*), 6.67 (1H, d, J = 7.9 Hz, Ar*H*), 3.72 (3H, OCH_3), 2.91 (1H, app sextet, J = 6.5 Hz, ArC*H*), 2.77 - 2.53 (2H, m, $ArCH_2$), 1.94 - 1.82 (2H, m, $ArCH_2CH_2$), 1.82 - 1.67 (1H, m, ArCHC*H*H), 1.60 - 1.49 (1H, m, ArCHCH*H*), 1.29 (3H, d, J = 7.0 Hz, $CHCH_3$);

^{13}C NMR δ_C (75 MHz, $CDCl_3$) 167.4 (s), 157.2 (s), 143.7 (s), 125.9 (d), 120.6 (d), 106.8 (d), 55.4 (q), 32.7 (d), 31.0 (t), 23.6 (t), 23.0 (q), 19.7 (t); **HRMS** (EI) $[M]^+$ found: 176.1201; $C_{12}H_{16}O$ requires 176.1201; **LRMS** (EI) 176 (60%, $[M]^+$), 175 (35%), 161 (70%, $[M\text{-}Me]^+$), 144 (100%, $[M\text{-}MeOH]^+$), 117 (40%), 91 (80%), 49 (95%).

2,2-Dimethyl-5-methoxy-1,2,3,4-tetrahydronaphthalene **10**

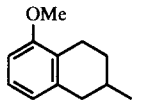


Method A :- 2,2-dimethyl-7-methoxy-1,2,3,4-tetrahydronaphthalene **9** (105 mg, 0.55 mmol), chloroform (20 mL), $ZrCl_4$ (645 mg, 2.77 mmol), 8 days, gave **10** (trace, <10%).

Method B :- 2,2-dimethyl-7-methoxy-1,2,3,4-tetrahydronaphthalene **9** (79 mg, 0.42 mmol), dichloromethane (5 mL), $ZrCl_4$ (485 mg, 2.08 mmol), 16h, gave **10** (71 mg, 0.37 mmol, 90%).

Data: a yellow oil; **IR** (neat) ν_{max} 2950 (m), 2905 (w), 2840 (w), 1585 (m), 1470 (s), 1440 (w), 1255 (s), 1090 (s), 765 (s), 670 (s) cm^{-1}; **UV** (MeOH) λ_{max} 277 (1210), 271 (1160), 233 (1080) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.11 (1H, app t, J = 7.9 Hz, Ar*H*), 6.70 (1H, d, J = 7.4 Hz, Ar*H*), 6.69 (1H, d, J = 8.1 Hz, Ar*H*), 3.85 (3H, s, OCH_3), 2.70 (2H, t, J = 6.8 Hz, $ArCH_2CH_2$), 2.56 (2H, s, $ArCH_2C$), 1.59 (2H, t, J = 6.8 Hz, $ArCH_2CH_2$), 1.00 (6H, s, $C(CH_3)_2$; **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.4 (s), 138.0 (s), 126.0 (d), 124.7 (s), 121.9 (d), 106.8 (d), 55.3 (q), 43.7 (t), 35.6 (t), 29.2 (s), 28.1 (2 x q), 20.9 (t); **HRMS** (EI) found: $[M]^+$, 190.1358; $C_{13}H_{18}O$ requires 190.1358; **LRMS** (EI) 190 (50%, $[MH]^+$), 175 (10%, $[M\text{-}CH_3]^+$), 134 (100%, $[M\text{-}CH_2C(CH_3)_2]^+$), 104 (30%), 91 (13%).

5-Methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **12**

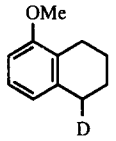


Method A :- 7-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **11** (90 mg, 0.51 mmol), $CHCl_3$ (20 mL), $ZrCl_4$ (600 mg, 2.58 mmol), 8 days, gave a 3:2 mixture (82 mg, 0.47 mmol) of **12** (54%) and **11** (36%).

Method B :- 7-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **11** (102 mg, 0.58 mmol), dichloromethane (20 mL), $ZrCl_4$ (596 mg, 2.56 mmol), 12 h, gave **12** (72 mg, 0.41 mmol, 71%).

Data: a colourless oil; **IR** (neat) υ_{max} 2950 (m), 2920 (s), 2835 (m), 1585 (s), 1470 (s), 1440 (m), 1260 (s), 1105 (s), 1080 (m), 765 (s) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 279 (1110), 270 (1150), 234 (2070) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.09 (1H, app t, J = 7.9 Hz, Ar*H*), 6.70 (1H, d, J = 7.4 Hz, Ar*H*), 6.67 (1H, d, J = 8.1 Hz, Ar*H*), 3.83 (3H, s, OCH_3), 2.93 - 2.76 (2H, m, $ArCHHCH_2CHCHH$), 2.65 - 2.47 (1H, m, $ArCHHCH_2$), 2.41 (1H, app ddquin, $ArCHHCH$), 1.98 - 1.74 (2H, m, $CHHCHCH_3$), 1.35 (1H, ddd, J = 12.9, 11.0, 5.9 Hz, $ArCH_2CHH$), 1.06 (3H, d, J = 6.6 Hz, $CHCH_3$); **^{1}H-^{1}H COSY** was used to establish the assignments given above; **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.5 (s), 138.5 (s), 125.9 (d), 125.7 (s), 121.5 (d), 106.9 (d), 55.4 (q), 38.4 (t), 32.2 (t), 28.9 (d), 23.3 (t), 20.0 (q); **HRMS** (EI) found: $[M]^+$ 176.1188, $C_{12}H_{16}O$ requires 176.1188; **LRMS** (EI), 176 (80%, $[M]^+$), 161 (100%, $[M\text{-}CH_3]^+$), 148 (20%), 134 (25%, $[M\text{-}CH_2CHCH_3]^+$).

1-Deutero-5-methoxy-1,2,3,4-tetrahydronaphthalene **14**



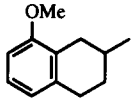
Method A :- 1-deutero-7-methoxy-1,2,3,4-tetrahydronaphthalene **13** (156 mg, 0.96 mmol), chloroform (12 mL), $ZrCl_4$ (1.06 g, 4.55 mmol), 2 days, yielded **14** (96 mg, 0.56 mmol, 62%).

Method B :- 1-deutero-7-methoxy-1,2,3,4-tetrahydronaphthalene **13** (70 mg, 0.43 mmol), dichloromethane (5 mL), $ZrCl_4$ (500 mg, 2.15 mmol), 3h, yielded **14** (57 mg, 0.35 mmol, 81%).

Data: A yellow oil; **IR** υ_{max} 2930 (s), 2860 (w), 2835 (w), 1585 (s), 1470 (s), 1250 (s), 1105 (s), 781 (m) cm^{-1}; **UV** λ_{max} (ε) 280 (7800), 270 (7400), 235 (8100) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.14 (1H, app t, J = 7.9 Hz, Ar*H*), 6.77 (1H, d, J = 7.7 Hz, ArH), 6.71 (1H, d, J = 8.1 Hz, Ar*H*), 3.87 (3H, s, OCH_3), 2.80 (1H, br, Ar*CH*D, 2.72 (2H, app t, J = 6.2 Hz, $ArCH_2$), 1.91 - 1.74 (4H, m, CH_2CH_2CHD; **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.5 (s), 138.6 (s), 126.1 (s), 125.9 (d), 121.6 (d), 106.9 (d), 55.4 (q), 29.5 (d of 1:1:1 t, J_{CD} = 28.3 Hz), 23.3 (t), 23.0 (t);

HRMS (EI), found: $[M]^+$, 163.1110; $C_{11}H_{13}OD$ requires 163.1110; **LRMS** (EI) 163 (51%, $[M]^+$), 148 (100%, $[M\text{-}CH_3]^+$), 135 (30%, $[M\text{-}CH_2CH_2]^+$), 132 (34%, $[M\text{-}OMe]^+$), 105 (25%), 92 (33%).

8-Methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **16**

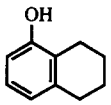


Method A :- 6-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **15** (325 mg, 1.85 mmol), chloroform (25 mL), $ZrCl_4$ (2.15 g, 9.23 mmol), 8 days, gave **16** (101 mg, 0.57 mmol, 31%) and a 4:1 mixture (163 mg, 0.93 mmol) of **16** (40%) and **15** (10%).

Method B :- 6-methoxy-2-methyl-1,2,3,4-tetrahydronaphthalene **15** (170 mg, 0.97 mmol), dichloromethane (15 mL), $ZrCl_4$ (1.04 g, 4.46 mmol), 16h, gave **16** (121 mg, 0.69 mmol, 71%).

Data: A colourless oil; **IR** (neat) υ_{max} 3000 (w), 2920 (s), 2835 (m), 1585 (s), 1470 (s), 1440 (s), 1250 (s), 1105 (s), 1060 (s), 1020 (m), 760 (s), 710 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 279 (1360), 270 (1310), 230 (3120) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.09 (1H, app t, J = 7.9 Hz, Ar*H*), 6.73 (1H, d, J = 7.7 Hz, Ar*H*), 6.67 (1H, d, J = 8.1 Hz, Ar*H*), 3.82 (3H, OCH_3), 2.96 (1H, ddd, J = 17.3, 4.8, 1.8 Hz, ArC*H*HCH), 2.86 (2H, 4 intense lines, second order A_2MX or ABMX, $ArCH_2CH_2$), 2.16 (1H, app ddq, J = 17.3, 10.3, 1.0 Hz, ArCH*H*CH), 1.94 - 1.76 (2H, m, $ArCH_2CHHCH$), 1.40 (1H, ddt, J = 12.5, 11.0, 8.4 Hz, $ArCH_2CHH$), 1.29 (3H, d, J = 6.3 Hz, $CHCH_3$); **^{1}H-^{1}H COSY** was used to establish the assignment given above; **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.4 (s), 138.3 (s), 126.0 (s), 125.9 (d), 121.4 (d), 106.9 (d), 55.4 (q), 31.9 (t), 29.8 (t), 29.6 (t), 29.2 (d), 22.5 (q); **HRMS** (EI) found: $[M]^+$, 176.1201; $C_{12}H_{16}O$ requires 176.1201; **LRMS** (EI) 177 (16%), 176 (91%, $[M]^+$), 161 (10%, $[M\text{-}Me]^+$), 148 (9%), 134 (100%, $[M\text{-}CH_2CHCH_3]^+$), 121 (11%), 115 (11%), 91 (17%).

5-Hydroxy-1,2,3,4-tetrahydronaphthalene **18**



Method A :-6-hydroxy-1,2,3,4-tetrahydronaphthalene **17** (95 mg, 0.64 mmol), dichloromethane (5 mL), $ZrCl_4$ (750 mg, 3.22 mmol), LiCl (134 mg, 3.2 mmol), 20 h, yielded recovered **17** (38 mg, 0.26 mmol, 40%) and **18** (36 mg, 0.24 mmol, 38%).

Method B :-6-hydroxy-1,2,3,4-tetrahydronaphthalene **17** (45 mg, 0.30 mmol), dichloromethane (5 mL), $ZrCl_4$ (375 mg, 1.61 mmol), 8h, yielded **18** (34 mg, 0.23 mmol, 75%). Data exhibited were identical to that exhibited by a commercial sample:[21] pale yellow solid; **m.p.** 69-70°C (Lit.[21] 69-71°C); **Mixed m.p.** 68-70°C; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 7.01 (1H, app t, J = 7.9 Hz, C-7*H*), 6.71 (1H, d, J = 7.4 Hz, Ar*H*), 6.63 (1H, J = 7.4 Hz, Ar*H*), 4.84 (1H, s, O*H*), 2.78 (2H, t, J = 6.1 Hz, $ArCH_2$), 2.66 (2H, t, J = 6.3 Hz, $ArCH_2$), 1.75 (4H, m, CH_2CH_2).

OTHER KEY EXPERIMENTS

2-(3-(4-Methoxyphenyl)-prop-1-yl)-tetrahydrofuran **3** with zirconium tetrachloride

To a stirred solution of 2-(3-(4-methoxyphenyl)-prop-1-yl)-tetrahydrofuran **3** (89 mg, 0.37 mmol) in dichloromethane (5 mL) was added zirconium tetrachloride (430 mg, 1.85 mmol). The reaction was stirred at ambient temperature for 24 h then poured into water (40 mL) and extracted with dichloromethane (3 x 15 mL). The combined organic extracts were dried ($MgSO_4$), concentrated at reduced pressure and the components separated by column chromatography (gradient elution, 10 - 60% Et_2O in petrol) to give firstly 7-methoxy-2,3,3a,4,5,6-hexahydro-1*H*-phenalene **5** (8 mg, 0.04 mmol, 10%); a pale yellow oil; **IR** (neat) υ_{max} 2920 (s), 2845 (m), 1650 (m), 1480 (w), 1460 (m), 1250 (m), 1110 (w), 825 (m) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 278 (850), 234 (1620) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 6.92 (1H, d, J = 8.5 Hz, Ar*H*), 6.67 (1H, d, J = 8.5 Hz, Ar*H*), 3.72 (3H, s, OCH_3), 2.90 - 2.75 (3H, m, ArC*H* + $ArCH_2$), 2.66 - 2.52 (2H, m, $ArCH_2$), 2.07 - 1.85 (3H, m), 1.85 - 1.62 (2H, m), 1.29 - 1.10 (3H, m); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 126.1 (d), 107.5 (d), 55.5 (q), 37.2 (d), 30.8 (t),

30.6 (t), 29.0 (t), 23.6 (t), 23.1 (t), 22.6 (t), quaternary centres not observed; **HRMS** (CI, NH_3) found: $[MH]^+$, 203.1436; $C_{14}H_{19}O$ requires 203.1436; **LRMS** (APCI) 203 (90%, $[MH]^+$), 185 (100%), 145 (20%), 130 (20%). Then 1-(3-hydroxyprop-1-yl)-5-methoxy-1,2,3,4-tetrahydronaphthalene **6** (26 mg, 0.12 mmol, 34%); a colourless oil; **IR** (neat) υ_{max} 3360 (br s), 2930 (s), 2850 (w), 1580 (m), 1465 (s), 1435 (m), 1250 (m), 1095 (m), 1070 (m), 775 (w) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 268 (1660), 257 (1850) nm; **^{1}H NMR** δ_H (360 MHz, $CDCl_3$) 7.12 (1H, app t, J = 7.7 Hz, Ar*H*), 6.82 (1H, dd, J = 7.7, 1.1 Hz, Ar*H*), 6.68 (1H, dd, J = 7.7, 1.1 Hz, Ar*H*), 3.82 (3H, s, OCH_3), 3.69 (2H, app t, J = 6.1 Hz, CH_2OH), 2.86 (1H, app dq, 8.6, 4.3 Hz, ArC*H*), 2.71 (1H, app dt, J = 17.1, 5.0 Hz, ArC*H*H), 2.60 (1H, ddd, J = 17.1, 8.4, 5.6 Hz, ArCH*H*), 1.91 -1.55 (9H, m); **^{1}H-^{1}H COSY** (300 MHz, $CDCl_3$) was used to establish the assignments given above; **n.O.e.** (360 MHz, $CDCl_3$) Irradiation at δ_H 6.82 (Ar*H*) caused a n.O.e. enhancement at δ_H 7.12 (Ar*H*) and 2.86 (ArC*H*), irradiation at δ_H 6.68 (Ar*H*) caused a n.O.e. enhancement at δ_H 7.12 (Ar*H*) and 3.82 (OCH_3), irradiation at δ_H 3.82 (OCH_3) caused a n.O.e. enhancement at δ_H 6.68 (Ar*H*), irradiation at δ_H 2.86 (ArC*H*) caused a n.O.e. enhancement at δ_H 6.82 (Ar*H*); **^{13}C NMR** δ_C (75 MHz, $CDCl_3$) 157.3 (s), 142.6 (s), 126.0 (s), 125.8 (d), 121.1 (d), 106.9 (d), 63.4 (t), 55.4 (q), 37.6 (d), 32.8 (t), 30.8 (t), 26.9 (t), 23.3 (t), 19.0 (t); **HRMS** (CI, NH_3) $[MH]^+$ found: 221.1542, $C_{14}H_{21}O_2$ requires 221.1542; **LRMS** (CI, NH_3), 238 (68%, $[M+NH_4]^+$), 221 (100%, $[MH]^+$), 203 (20%, $[MH-H_2O]^+$), 161 (15%). And finally 1-(3-hydroxyprop-1-yl)-7-methoxy-1,2,3,4-tetrahydronaphthalene **4** (35 mg, 0.16 mmol, 43%);[3] a colourless oil; **IR** (neat) υ_{max} 3335 (br m), 2930 (s), 2850 (m), 1610 (m), 1500 (s), 1455 (m), 1250 (m), 1040 (s) cm^{-1}; **UV** (MeOH) λ_{max} (ε) 287 (1070), 279 (1200), 232 (1430) nm; **^{1}H NMR** δ_H (300 MHz, $CDCl_3$) 6.99 (1H, d, J = 8.3 Hz, Ar*H*), 6.72 (1H, d, J = 2.8 Hz, Ar*H*), 6.69 (1H, dd, J = 8.3, 2.8 Hz, Ar*H*), 3.80 (3H, s, OCH_3), 3.68 (2H, t, J = 6.5 Hz, CH_2OH), 2.80 - 2.70 (1H, m, ArC*H*), 2.74 - 2.66 (2H, m, $ArCH_2$), 1.90 - 1.39 (9H, m); **^{1}C NMR** δ_C (75 MHz, $CDCl_3$) 157.6 (s), 142.4 (s), 130.0 (d), 129.5 (s), 113.7 (d), 111.6 (d), 63.4 (t), 55.4 (q), 37.8 (d), 32.9 (t), 30.7 (t), 29.1 (t), 27.6 (t), 20.2 (t); **HRMS** (CI, NH_3) $[MH]^+$ found: 221.1542, $C_{14}H_{21}O_2$ requires 221.1542; **LRMS** (EI), 220 (50%, $[M]^+$), 174 (13%, $[M-CH_2CH_2OH_2]^+$), 161 (100%, $[M-(CH_2)_3OH]^+$), 146 (10%), 134 (14%).

1-(3-Hydroxyprop-1-yl)-7-methoxy-1,2,3,4-tetrahydronaphthalene **4** with zirconium(IV) chloride

To a stirred solution of 1-(3-hydroxyprop-1-yl)-7-methoxy-1,2,3,4-tetrahydronaphthalene **4** (222 mg, 1.00 mmol) in dichloromethane (20 mL) was added zirconium tetrachloride (1.20 g, 5.15 mmol). The reaction was stirred at ambient temperature for 2 days then poured into water (100 mL) and extracted with dichloromethane (2 x 50 mL). The combined organic extracts were dried ($MgSO_4$), concentrated at reduced pressure and the components separated by column chromatography (gradient elution, 10 - 60% Et_2O in petrol) to give firstly 7-methoxy-2,3,3a,4,5,6-hexahydro-1*H*-phenalene **5** (20 mg, 0.10 mmol, 10%), then 1-(3-hydroxyprop-1-yl)-5-methoxy-1,2,3,4-tetrahydronaphthalene **6** (147 mg, 0.67 mmol, 67%); and finally recovered starting material **4** (27 mg, 0.12 mmol, 12%). Data as quoted above.

6-Methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene **19** with zirconium(IV) chloride

To a stirred solution of **19** (102 mg, 0.58 mmol) in chloroform (5 mL) was added $ZrCl_4$ (675 mg, 2.90 mmol). After 4 days the reaction was poured into water (20 mL) and extracted with dichloromethane (3 x 40 mL). The combined organic phases were dried ($MgSO_4$) and evaporated at reduced pressure. Column chromatography (neat petrol) gave an inseparable 1:1 mixture (90 mg, 0.50 mmol) of **19** (40%) and **20** (40%). Data as quoted above.

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